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Properties of dimers

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Contents

Abstract. Current spectroscopic data on dimers (molecules consisting of two similar atoms) and their ions are presented and analysed. Methods for obtaining such data are discussed.

1. Introduction

Collection and analysis of information about the properties of concrete physical systems, parameters of interactions in them and transitions occurring between their states occupy a certain place in the practice of each scientist. In the case of plasma and gaseous systems this information concerns partially the parameters of atoms, molecules, and ions, as well as characteristics of transitions between their states. The present review is devoted to one of such systems — dimers, i.e. homonuclear diatomic molecules containing atoms of one element, and also to dimer ions. Notice that for a specialist it is of importance just as the magnitude of a certain parameter, so an accuracy and reliability pertaining to this magnitude. To estimate the accuracy, a closer look at the methods of parameter determination is called for. Appropriate analysis is one of the goals of this review.

When examining spectroscopic parameters of diatomic molecules, mention should be necessarily made of the Huber and Herzberg classic book [1], which summed up previous results and elaborated a simple method of representing the data involved. The material of this book supplemented with new results forms the basis for various reviews and reference books concerning the molecular parameters. In particular, the authors of reviews [2, 3] collected and analyzed information about dimer parameters which was drastically updated during the last decade. In the discussion which follow this new information is provided with accounting for its accuracy and reliability. This being so, in the present review we, on the one hand, concentrate upon methods of obtaining quantitative information of interest and, on the other hand, consider main parameters and systems, thus trying to gather uniform data on dimers.

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2. Quantum numbers and parameters of dimers

Let us consider, first, the behaviour of electronic terms of dimers and their quantum numbers. Quantum numbers of molecular terms of dimers depend on the rules of summing the electronic momenta into the total molecular momentum. They are determined by relationship between three various interactions in a molecule: V_e — the interaction potential between the orbital angular momentum and molecular axis, V_m — the interaction potential between the orbital and spin momenta, V_r — the interaction potential between electrons and rotation al motion of the molecule. Depending on the quantitative relationship between above potentials, one can rely on a certain method of determining molecular eigen states [4]. Exhausting different possible relationships between the above interaction potentials, one can arrive at different types of so-called Hund's coupling cases. In doing so, a certain set of molecular quantum numbers is attached to each Hund's coupling case. Within the framework of this classical scheme [4 – 6], we assume the interaction potential between the electrons and rotational motion of the molecule to be relatively weak which conforms to not strongly excited molecules. Then the limit $V_e \gg V_m$ corresponds to the Hund's coupling case 'a', while $V_e \ll V_m$ is consistent with the Hund's case 'c'.

In the Hund's coupling case 'a', the projection of the electronic angular momentum onto the molecular axis and the total molecular spin comprise the quantum numbers of the molecule. Projections of the electronic angular momentum are denoted by Greek capital letters Σ, Π, Δ, Φ, Γ pertaining to their absolute values of 0, 1, 2, 3, 4 in units of $h/2\pi$, correspondingly. In the Hund's coupling case 'c', the projection of the total molecular momentum onto its axis comprises the sole quantum number which is denoted by a

cipher. If the projection of the appropriate momentum onto the molecular axis equals zero, there appears one more symmetry transformation incident to reflection of electrons in the symmetry plane going through the axis. If the wave function of electrons conserves the sign under that reflection, this state is marked by Σ^+, if it changes the sign, the state is marked by Σ^-.

The dimer as a diatomic molecule consisting of identical atoms possesses an additional symmetry due to reflection of electrons in the plane which is perpendicular to the molecular axis and bisects it. The interaction potential of electrons does not change as a result of this transformation. If the electronic wave function conserves the sign as a result of electron reflection in the symmetry plane, the electronic state is even; otherwise the electronic state is odd. Since the electronic Hamiltonian is invariant under inversion of electrons, it is convenient to connect the electron parity just with the electron inversion. Then if the electronic wave function retains its sign under the electron inversion with respect of the molecular centre, this dimer state is even and is labelled by 'g'(gerade); if the electron inversion changes the sign of the electronic wave function, this state is odd and labelled by 'u'(ungerade). Below we will rely on this definition of the dimer parity.

There occurs certain correlation between quantum numbers of a dimer and states of atoms from which it is formed. For example, in the Hund's coupling case 'a', the atomic state is characterised by an angular momentum and the total electronic spin, and interaction between electrons of different atoms leads to splitting of the energy levels dependent of the projection of an electronic orbital momentum onto the molecular axis. Interaction of two atoms with the same quantum numbers causes mixing of these states, and if the interaction between electrons of different atoms exceeds remarkably the spin-orbit splitting of atomic levels, the total spin of electrons and the projection of the total electronic momentum onto the molecular axis make quantum numbers of interacting atoms. Then interaction between atoms does not change the total number of states in this system, but a number of electronic terms, i.e. a number of states of a various energy, can be different in the cases of free and interacting atoms. Constructing the molecular wave functions from atomic ones in the case of a weak interaction between atoms, one can ascertain the character of quantum numbers in the molecule, the symmetry and number of molecular electronic terms. In particular, Tables 1, 2 contain electronic terms of the molecule consisting of two identical atoms for the Hund's coupling cases under consideration [7, 8].

Let us analyze the character of bond formation in the limit of a weak atomic interaction in the another context. If atoms interact weakly, that is, the distance between them is large, the interaction potential of atoms may be divided into two parts — long-range and exchange ones [9]. A long-range potential is determined by interaction of electrical momenta of atoms induced under their relative motion. This interaction respects usually to attraction forces and its potential energy depends on the distance between atoms by an inverse power law. The exchange interaction potential is determined by overlapping of electron wave functions corresponded to different atoms, and hence decreases by an exponential law with removal of atoms. Just this part of atomic interaction is responsible for making the chemical bond between atoms. The sign of the exchange interaction depends on the state symmetry. For example, in the case of interaction between two hydrogen atoms in the ground state or other identical atoms with a zero angular momentum and spin of 1/2, two states of the molecule are only possible — even and odd. The even state has the symmetry ${}^1\Sigma_g^+$ in the Hund's coupling case 'a' or 0_g^+ for the Hund's case 'c', and the exchange interaction leads to atomic attraction. In the odd state with the symmetry ${}^3\Sigma_u^+$ for the Hund's case 'a' or 1_u, 0_u^- for the Hund's case 'c', a repulsion of atoms takes place. Hence, a chemical bond exists only in one of these states. Roughly speaking, one half of electronic terms for interacting atoms corresponds to bound molecular states. These states are the object of our consideration. Notice that the above description of molecules was worked out in twenties — thirties at the dawn of the age of the quantum mechanics. It forms a basis for methods of analyzing the molecular parameters.

Table 1. Correlation between quantum numbers of two identical atoms and the dimer which they form in the Hund's coupling case 'a' [7, 8]. (A number of possible electronic terms of a given symmetry is given in parentheses if it is above one.)

Atomic state	Molecular state
${}^1S$	${}^1\Sigma_g^+$
${}^2S$	${}^1\Sigma_g^+$, ${}^3\Sigma_u^+$
${}^3S$	${}^1\Sigma_g^+$, ${}^3\Sigma_u^+$, ${}^5\Sigma_g^+$
${}^4S$	${}^1\Sigma_g^+$, ${}^3\Sigma_u^+$, ${}^5\Sigma_g^+$, ${}^7\Sigma_u^+$
${}^1P$	${}^1\Sigma_g^+(2)$, ${}^1\Sigma_u^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$
${}^2P$	${}^1\Sigma_g^+(2)$, ${}^1\Sigma_g^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$, ${}^3\Sigma_u^+(2)$, ${}^3\Sigma_g^-$, ${}^3\Pi_g$, ${}^3\Pi_u$, ${}^3\Delta_u$
${}^3P$	${}^1\Sigma_g^+(2)$, ${}^1\Sigma_u^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$, ${}^3\Sigma_u^+(2)$, ${}^3\Sigma_g^-$, ${}^3\Pi_g$, ${}^3\Pi_u$, ${}^3\Delta_u$, ${}^5\Sigma_g^+(2)$, ${}^5\Sigma_u^-$, ${}^5\Pi_g$, ${}^5\Pi_u$, ${}^5\Delta_g$
${}^4P$	${}^1\Sigma_g^+(2)$, ${}^1\Sigma_g^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$, ${}^3\Sigma_u^+(2)$, ${}^3\Sigma_g^-$, ${}^3\Pi_g$, ${}^3\Pi_u$, ${}^3\Delta_u$, ${}^5\Sigma_g^+(2)$, ${}^5\Sigma_u^-$, ${}^5\Pi_g$, ${}^5\Pi_u$, ${}^5\Delta_g$, ${}^7\Sigma_u^+(2)$, ${}^7\Sigma_g^-$, ${}^7\Pi_g$, ${}^7\Pi_u$, ${}^7\Delta_u$
${}^1D$	${}^1\Sigma_g^+(3)$, ${}^1\Sigma_u^-(2)$, ${}^1\Pi_g(2)$, ${}^1\Pi_u(2)$, ${}^1\Delta_g(2)$, ${}^1\Delta_u$, ${}^1\Phi_g$, ${}^1\Phi_u$, ${}^1\Gamma_g$
${}^2D$	${}^1\Sigma_g^+(3)$, ${}^1\Sigma_u^-(2)$, ${}^1\Pi_g(2)$, ${}^1\Pi_u(2)$, ${}^1\Delta_g(2)$, ${}^1\Delta_u$, ${}^1\Phi_g$, ${}^1\Phi_u$, ${}^1\Gamma_g$, ${}^3\Sigma_u^+(3)$, ${}^3\Sigma_g^-(2)$, ${}^3\Pi_u(2)$, ${}^3\Pi_g(2)$, ${}^3\Delta_g$, ${}^3\Delta_u(2)$, ${}^3\Phi_g$, ${}^3\Phi_u$, ${}^3\Gamma_u$
${}^3D$	${}^1\Sigma_g^+(3)$, ${}^1\Sigma_u^-(2)$, ${}^1\Pi_g(2)$, ${}^1\Pi_u(2)$, ${}^1\Delta_g(2)$, ${}^1\Delta_u$, ${}^1\Phi_g$, ${}^1\Phi_u$, ${}^1\Gamma_g$, ${}^3\Sigma_u^+(3)$, ${}^3\Sigma_g^-(2)$, ${}^3\Pi_u(2)$, ${}^3\Pi_g(2)$, ${}^3\Delta_g$, ${}^3\Delta_u(2)$, ${}^3\Phi_g$, ${}^3\Phi_u$, ${}^3\Gamma_u$, ${}^5\Sigma_g^+(3)$, ${}^5\Sigma_u^-(2)$, ${}^5\Pi_g(2)$, ${}^5\Pi_u(2)$, ${}^5\Delta_g(2)$, ${}^5\Delta_u$, ${}^5\Phi_g$, ${}^5\Phi_u$, ${}^5\Gamma_u$

Table 2. Correlation between quantum numbers of two identical atoms and the dimer which they form in the Hund's coupling case 'c' [7, 8]. (A number of possible electronic terms of a given symmetry is given in parentheses if it is above one.)

Atom	Dimer
$J = 0$	0_g^+
$J = 1/2$	1_u, 0_g^+, 0_u^-
$J = 1$	2_g, 1_u, 1_g, $0_g^+(2)$, 0_u^-
$J = 3/2$	3_u, 2_u, 2_g, $1_u(2)$, 1_g, $0_g^+(2)$, $0_u^-(2)$
$J = 2$	4_g, 3_u, 3_g, $2_u z$, $2_g(2)$, $1_u(2)$, $1_g(2)$, $0_g^+(3)$, $0_u^-(2)$

3. Parameters of diatomics

The emergence of molecular spectroscopy led not only to certain concepts concerning the molecular properties, but also to universally recognised notation as well as units in which the spectroscopic parameters of molecules are

expressed. Below we shall follow them. Considering not highly-excited states of molecules, one can assume in the zero-order approximation of a perturbation theory the electronic, vibration and rotation degrees of freedom to be independent, and allow for their interaction as a perturbation. Then a molecular state can be defined by a symmetry of its electronic term, by a vibrational quantum number v and rotational quantum number J, where v and J are the integers. Correspondingly, the molecular excitation energy is given by the formula

$$E = T_e + G(v) + F_v(J), \tag{1}$$

where T_e is the electronic excitation energy of the term, $G(v)$ is the vibrational energy, and $F_v(J)$ is the rotational energy. The above formula corresponds to the zero approximation in the expansion of the molecular energy over a small parameter of the theory pertaining to a weak interactions between electron, vibration and rotation sub-systems in the molecule. This approach makes possible to derive the molecular parameters whose values will be given in the tables below. In the framework of this approximation we assume the excitation energy of the electronic term T_e to be independent neither of the vibration nor of the rotation quantum numbers. The vibrational energy $G(v)$ does not depend on the rotational excitation and takes the form:

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2, \tag{2}$$

where ω_e is the harmonic oscillator energy, and $\omega_e\, x_e$ is the oscillator anharmonic parameter. Of course, these parameters are determined by properties of the electronic term to which they relate. The rotational energy of the molecule is reported as follows:

$$F_v(J) = B_v J(J+1), \qquad B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right). \tag{3}$$

Here B_v is the rotational constant and the parameter α_e characterises its dependence on the vibration quantum number. By definition, the rotational constant of the diatomic molecule is expressed through the moment of inertia of a rotating molecule with the aid of the formula [4]: $B = \hbar^2/(2\mu r^2)$, where $\hbar$ is the Plank constant$/2\pi$, μ is the reduced mass of nuclei, r is the equilibrium internuclear distance. For the unexcited vibrational and rotational state, this distance is denoted by r_e.

Parameters of expansion of the molecular energy refer to certain quantum numbers. In accordance with the spectroscopic method of their determination, all the parameters T_e, ω_e, $\omega_e x_e$, B_e, α_e are traditionally expressed in units of cm^{-1}. Sometimes additional parameters of the molecule are introduced which take into account further corrections to the expansion of the energy over a small parameter of the perturbation theory. These corrections account for the dependence of the rotational constant on the rotational excitation or the next in order terms of the energy expansion over the oscillator anharmonicity. Below we shall restrict ourselves to the introduced parameters only and entertain the above scheme of the energy expansion. Note the useful relationship between the rotational constant and the equilibrium distance between nuclei which assumes the form :

$$B = \frac{16.858}{\mu r^2}, \tag{4}$$

where the reduced mass of nuclei μ is expressed in atomic mass units and the distance between nuclei r is given in A. The inverse relation between these quantities is

$$r = \frac{4.1058}{\sqrt{\mu B}}. \tag{5}$$

According to formula (2), the distance between adjacent vibrational levels in a diatomic molecule

$$\Delta G\left(v + \frac{1}{2}\right) = G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1)$$

decreases with a rise in excitation of the molecule because the difference between the widths of potential wells for a real molecule and the corresponding harmonic oscillator increases with excitation enhancement for the molecule. In the long run the quantity $\Delta G(v + 1/2)$ tends to zero that corresponds to the onset of molecular dissociation. Then according to formula (2) with an accuracy of the first term of expansion over the small parameter $\omega_e x_e/\omega_e$, the dissociation energy of the molecule is equal to

$$D_0 = \frac{\omega_e^2}{4\omega_e x_e}. \tag{6}$$

But formula (6) constitutes rough approximation because expansion (2) is valid for weak excitations when the anharmonism contribution into the excitation energy is small. Therefore, it is desirable to rely on the real distances between neighbouring energy levels in determination of the molecular dissociation energy. It is put into effect in the simple and convenient method by Birge and Sponer [10] which uses the graphical dependence of the variable $\Delta G(v + 1/2)$ on the vibrational quantum number v. An appropriate approximation of this dependence into the region of v where this function becomes zero allows us to determine a number of vibrational levels for an electronic term considered. And an area enclosed by the curve at hand gives the molecular dissociation energy. Fig.1 illustrates this method as for the hydrogen molecule in the ground state [11].

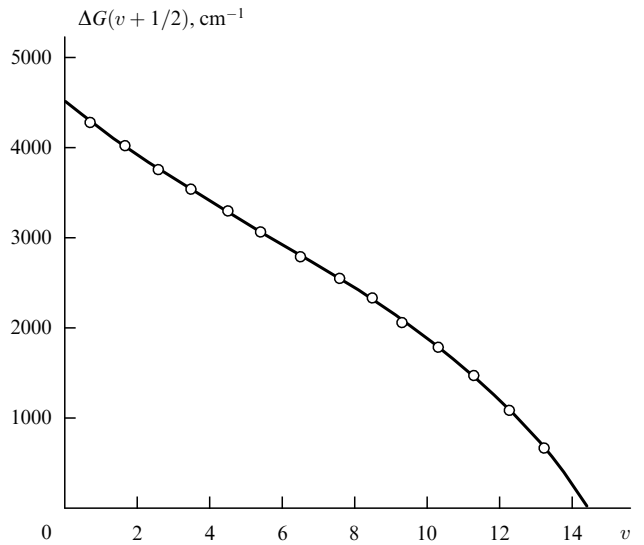

Figure 1. Dependence of the energy difference between adjacent vibrational levels on the vibrational number v for the hydrogen molecule [11]. The area enclosed by this curve equals the dissociation energy of the hydrogen molecule. This illustrates the Birge–Sponer method.

The Birge–Sponer method is widely practiced for determining the molecular dissociation energy by processing the spectroscopic data. Notice that along with the dissociation energy of the ground vibrational state of the molecule D_0, the quantity $D_e = D_0 + \hbar\omega_e/2$ is used as the molecular parameter which defines the energy difference between the bottom of the potential well and the boundary of dissociation. The latter is a convenient characteristic of the molecular electronic term.

4. Dimers in the ground state

The main information about dimers correspond to the ground electronic state of the molecules. These data are given in Table 3. The accuracy of data and methods of determining the dimer parameters depend on the molecular sort so that it is convenient to divide dimers into the following groups. In the first group we include dimers which exist in the gaseous phase in the form of diatomics under the normal conditions (as, for example, molecules H_2, N_2, O_2), or these molecules are formed effectively in the gaseous phase under near conditions (as the halogen molecules Cl_2, F_2, etc.). In this case dimers in a gas or vapor make up the main or pronounced part of the substance. It simplifies study of these dimers, and spectroscopic methods are used in the first place for this aim. Some additional information concerning the dissociation energy and other energy parameters can be obtained on the basis of thermochemical approaches. Methods of the analysis of these molecules were in progress for any length of time, and a great body of information was gained. Data compiled in Table 3 for the homonuclear diatomic molecules have long been in use, and their revision concerns the escalated accuracy of parameters which is high enough for molecules of this group. Hence, within the limits of the accuracy which corresponds to parameters of other dimers, data of Table 3 do not differ radically from that of [1].

In the second group we include dimers of rare gas atoms, and also Mg_2, Ca_2, and Hg_2 so that these molecules consist of atoms with the closed electron shell. Then the exchange interaction of atoms corresponds to their repulsion, and the bond is supported by a weak long-range interaction of atoms.

Table 3. Spectroscopic parameters of homonuclear diatomic molecules in the ground state. (The reduced nuclear mass μ accounts for the natural isotopic composition of an element and is expressed in atomic mass units ($1\,\text{u} = 1.66056\times10^{-24}$ g).)

Dimer	Term	μ, u	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3}cm^{-1}	D, eV	References
Ag_2	$X\,^1\Sigma_g^+$	53.934	135.8	0.50	2.53	0.049	0.195	1.67	[16, 23 – 26, 229, 244]
Al_2	$X\,^3\Pi_u$	13.491	284.2	2.02	2.47	0.205	0.8	0.46	[27 – 29, 235]
Ar_2	$X\,^1\Sigma_g^+$	19.974	30.68	2.42	3.76	0.0596	3.64	0.012	[22, 30 – 34]
As_2	$X\,^1\Sigma_g^+$	37.461	429.6	1.12	2.103	0.102	0.333	3.96	[35, 36, 240, 242]
Au_2	$X\,^1\Sigma_g^+$	98.483	190.9	0.42	2.47	0.028	0.066	2.31	[26, 37 – 39, 229]
B_2	$X\,^3\Sigma_g^-$	5.405	1059	15.66	1.60	1.216	14.0	2.8	[40 – 42]
Ba_2	$X\,^1\Sigma_g^+$	68.665	84.1	0.16	4.6	0.009	0.084	—	[43, 44]
Be_2	$X\,^1\Sigma_g^+$	4.5061	275.8	12.5	2.45	0.615	81	0.098	[45 – 47]
Bi_2	$X\,^1\Sigma_g^+$	104.49	173.1	0.376	2.66	0.023	0.053	2.08	[48–50, 190, 241]
Br_2	$X\,^1\Sigma_g^+$	39.952	325	1.08	2.28	0.082	0.318	2.05	[51 – 59, 225]
C_2	$X\,^1\Sigma_g^+$	6.0055	1855	13.27	1.24	1.899	17.8	5.36	[60 – 63, 225, 237]
Ca_2	$X\,^1\Sigma_g^+$	20.04	64.9	1.087	4.28	0.047	0.7	0.13	[64]
Cd_2	$X\,^1\Sigma_g^+$	56.205	22.5	0.4	5.1	0.011	—	0.040	[65, 66]
Cl_2	$X\,^1\Sigma_g^+$	17.726	559.7	2.68	1.99	0.244	2.1	2.576	[67 – 76, 225]
Co_2	$X\,^1\Sigma_g^+$	29.466	280	—	2.0	0.14	—	0.9	[77, 78, 227]
Cr_2	$X\,^1\Sigma_g^+$	25.998	470	14.1	1.68	0.23	3.8	1.66	[79 – 81]
Cs_2	$X\,^1\Sigma_g^+$	66.453	42.02	0.082	4.65	0.013	0.026	0.452	[82–87, 226]
Cu_2	$X\,^1\Sigma_g^+$	31.773	266.4	1.03	2.21	0.109	0.062	1.99	[26, 88 – 92, 230, 245]
F_2	$X\,^1\Sigma_g^+$	9.4992	916.6	11.24	1.41	0.89	14.1	1.66	[93 – 96, 225]
Fe_2	$X\,^1\Sigma_g^+$	27.924	412.0	1.4	2.02	0.148	—	0.9	[97 – 100, 227]
Ga_2	$X\,^3\Pi_u$	34.86	158	1.0	2.76	0.063	—	1.18	[101, 102]
Ge_2	$X\,^3\Sigma_g^-$	36.295	259	0.8	2.44	0.078	—	2.5	[103 – 105]
H_2	$X\,^1\Sigma_g^+$	0.5040	4401	121.3	0.741	60.85	3.062	4.478	[106 – 110]
D_2	$X\,^1\Sigma_g^+$	1.0070	3116	61.82	0.741	30.44	1.079	4.556	[111 – 113]
T_2	$X\,^1\Sigma_g^+$	1.5082	2546	41.23	0.741	20.34	589	4.591	—
He_2	$X\,^1\Sigma_g^+$	—	—	—	2.97	—	—	0.001	[114 – 117]
Hg_2	$X\,0_g^+$	100.30	18.5	0.27	3.65	0.013	—	0.055	[118 – 120]
I_2	$X\,^1\Sigma_g^+$	63.452	214.5	0.615	2.67	0.037	0.124	1.542	[121 – 129]
In_2	$X\,^3\Pi_u$	57.41	111	0.8	3.14	0.030	—	0.83	[130, 131]
K_2	$X\,^1\Sigma_g^+$	19.549	92.09	0.283	3.92	0.057	0.165	0.551	[132 – 136, 226]
Kr_2	$X\,^1\Sigma_g^+$	41.90	24.1	1.34	4.02	0.024	1.0	0.018	[22, 137 – 141]
Li_2	$X\,^1\Sigma_g^+$	3.571	351.4	2.59	2.67	0.672	7.04	1.05	[142 – 148]
Mg_2	$X\,^1\Sigma_g^+$	12.152	51.08	1.623	3.89	0.093	3.78	0.053	[149, 150]
Mn_2	$X\,^1\Sigma_g^+$	27.469	68.1	1.05	2.52	0.097	—	0.79	[151, 169]
Mo_2	$X\,^1\Sigma_g^+$	47.97	477	1.51	2.2	0.072	0.48	4.1	[152]
N_2	$X\,^1\Sigma_g^+$	7.0034	2359	14.95	1.098	1.998	17.1	9.579	[153 – 162]
Na_2	$X\,^1\Sigma_g^+$	11.495	159.1	0.725	3.08	0.155	0.874	0.731	[163 – 168, 226]

Table 3 (*continued*)

Dimer	Term	μ, u	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3}cm^{-1}	D, eV	References
Nb_2	$X\,^3\Sigma_g^-$	46.453	424.9	0.94	2.1	0.084	0.242	5.48	[169, 170]
Ne_2	$X\,^1\Sigma_g^+$	10.090	31.3	6.48	2.91	0.17	60	0.037	[141, 171, 172]
Ni_2	$X\,^3\Pi_u$	29.345	250	1.1	2.3	0.104	—	1.7	[173]
O_2	$X\,^3\Sigma_g^-$	7.9997	1580	11.98	1.207	1.445	15.93	5.12	[174 – 176, 225, 236]
P_2	$X\,^1\Sigma_g^+$	15.489	780.8	2.83	1.89	0.304	1.5	—	[177, 178, 225, 232]
Pb_2	$X\,^3\Sigma_g^-$	103.6	110.2	0.327	2.93	0.019	0.057	0.83	[179, 180, 204]
Pd_2	$X\,^3\Sigma_g^+$	53.21	159	—	2.48	0.051	—	0.76	[181]
Pt_2	$X\,^1\Sigma_g^+$	97.541	259.4	0.9	2.34	0.032	—	0.93	[182, 183]
Rb_2	$X\,^1\Sigma_g^+$	42.734	57.78	0.139	4.17	0.023	0.047	0.495	[184 – 186, 226, 243]
Rh_2	$X\,^5\Delta_u$	51.453	238	—	2.67	0.046	—	1.5	[187, 188]
S_2	$X\,^3\Sigma_g^-$	16.03	725.6	2.28	1.89	0.295	1.58	4.37	[189 – 191, 225, 234]
Sb_2	$X\,^1\Sigma_g^+$	60.825	269.9	0.58	2.34	0.050	11.2	3.09	[192, 241]
Sc_2	$X\,^5\Sigma_u^-$	22.478	238.9	0.93	2.21	0.153	—	1.69	[193, 194]
Se_2	$X\,^3\Sigma_g^-$	39.48	385.3	0.963	2.16	0.89	0.28	2.9	[195 – 199, 231]
Si_2	$X\,^3\Sigma_g^-$	14.043	510.9	2.02	2.24	0.239	1.35	3.24	[200 – 202, 233, 238]
Sn_2	$X\,^3\Sigma_g^-$	59.345	186.2	0.261	2.75	0.038	0.1	2.0	[203, 204]
Sr_2	$X\,^1\Sigma_g^+$	43.81	39.6	0.45	4.45	0.019	0.2	0.13	[205]
Te_2	$X\,^3\Sigma_g^-$	63.80	249.1	0.537	2.56	0.040	0.109	2.7	[169, 195, 206 – 208]
Ti_2	$X\,^3\Delta_g$	23.44	407.9	1.08	1.94	0.187	—	1.4	[193, 209, 210]
Tl_2	$X\,^3\Sigma_g^-$	102.19	80	0.5	3.0	0.018	—	0.001	[211]
V_2	$X\,^3\Sigma_g^-$	25.471	537.5	3.34	1.78	0.209	1.4	2.62	[169, 212, 213]
W_2	X	91.92	336.8	1.0	—	—	—	6.9	[214]
Xe_2	$X\,^1\Sigma_g^+$	65.645	21.12	0.65	4.36	0.013	0.3	0.024	[22, 139, 215 – 219]
Y_2	$X\,^1\Sigma_g^+$	44.453	206.5	—	2.8	0.048	—	1.6	[220, 239]
Zn_2	$X\,^1\Sigma_g^+$	32.69	25.7	0.60	4.8	0.022	—	0.034	[66, 221, 222]
Zr_2	$X\,^1\Sigma_u^+$	45.61	373	—	2.3	0.070	—	1.5	[209, 220, 223, 224]

Therefore, these molecules are ineffectively formed in gases or vapors whereas a gas or vapor consisting of atoms of these elements is open to inspection. In this instance information about parameters of atomic interaction potential can be gleaned from measurements of gaseous virial coefficients, critical parameters of gases or vapors, the saturated vapor pressures and other parameters of gases which are determined by interaction between atoms. For rate gas systems, a weak interaction between atoms takes place in their condensed phase, so that information about pair interaction potentials of atoms can be extracted from properties of rare-gas crystals and liquids, and also from parameters of transitions between these phases. Besides, parameters of atomic interaction in dimers for this group of elements can be found from measurements of the total and differential cross sections of scattering in beam experiments and also by measuring the transport coefficients, i.e. the coefficients of thermal conductivity and viscosity for these elements. The analysis of excitation spectra in these dimers is also of importance. The set of such measurements allows us to construct potential curves of atomic interaction for these elements in the ground states. In particular, contemporary data for the interaction potentials of two rare-gas atoms are presented in [12] for neon, in [13] for argon, in [14] for krypton, and in [15] for xenon. As for He_2, in this case the potential well depth is too little and the He_2 dimer does not form in the ground state. Thus, the second group of dimers is characterised by a shallow well for the interaction potential of atoms. In due course, the accuracy of data for these dimers improves but methods of their determination do not change appreciably.

Dimers of elements from the third group can be formed in vapors while these elements exist in the solid state under normal conditions. Then under optimal excitation conditions the dimers constitute only a small part of a vapor. Nevertheless, spectral investigations allow us to extract those transitions in dimers which yield required parameters both for the ground and excited states.

Though spectral methods for dimers of the first and third groups do not differ, the possibility of determining the dimer parameters depends both on the character of dimer generation and on operation characteristics of experimental tools including an instrumental resolution of spectral equipment. Hence, improvement of experimental techniques can be of importance in obtaining the isolated results.

Radiative transitions in some dimers from these groups are well resolved in excited vapors. It takes place, for example, in the dimers of alkali metals whose excited states are generated in a vapor so that spectral lines of separate electronic-vibrational-rotational transitions are detected and resolved with high reliability. On the contrary, in the case of heat-resistant materials, the revision is required both for methods of dimer generation and resolution of spectral lines emitted under transitions between states of these dimers. Because of these troubles, data for dimers of some metals are characterised by a low accuracy or do not exist yet.

A progress in study of these dimers is observed in the last decade as a result of creating the contemporary spectral devices and techniques based on the use of dye lasers. As a demonstration of possibility of these methods, Fig. 2 gives a scheme of experimental set-up for the analysis of parameters in Ag_2 [16].

The principal peculiarity of experimental procedures for these dimers is the generation of the latter in a beam expanding into a vacuum instead of that in an evaporation

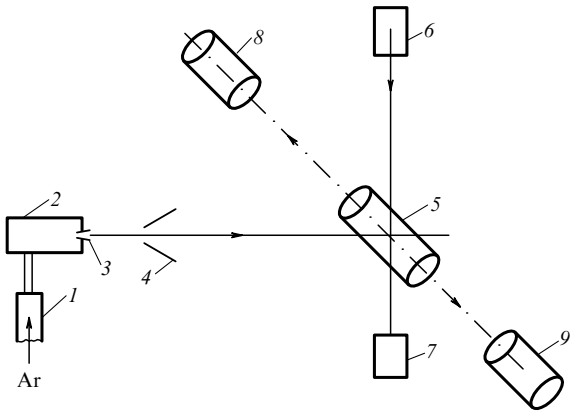

Figure 2. Schematics of experimental set-up for the spectral analysis of a silver dimer: *1* — the argon flux at the pressure upstream of 3 – 7 atm; *2* — an oven for silver vaporisation at the temperature up to 2000 K and the silver vapor pressure of 0.01 – 0.03 atm; *3* — a jet of diameter 60 μm; *4* — a skimmer; *5* — a cell of beam excitation; *6* — tuned lasers; *7* — a spectrometer; *8* — an electron multiplier; *9* — an ion multiplier.

cell. Though this technique is more complicated, it allows the experimenter to escape some distortions due to processes of vapor excitation and secondary processes in an evaporation cell. The dimer generation in beams occurs in nonequilibrium conditions, and for this reason the concentration of dimers in a beam is higher than that in an evaporation cell. In reality, the dimer concentration in beams depends on the ratio of time during which an expanding beam reaches a measurement cell, to the time of a condensation process which proceeds through a stage of dimer formation. Changing the pressures of vapor and buffer gas allows the finding of optimal conditions for the dimer concentration in the measurement cell.

There exist two methods of dimer generation. In the first one, which is illustrated in Fig. 2, a high-temperature oven is used for that generation. For heat-proof metals, the laser evaporation is more suitable. In so doing, evaporated metal atoms are trapped by an inert gas flow [17]. Free-jet expansion of this mixture leads to decrease in its temperature and causes the vapor condensation with forming the dimers on the first stage of the process. Hence, methods of dimer generation in the beams lead to reach high concentrations of dimers as compared to those in an evaporation cell.

We do not dwell here on spectral techniques which can encompass the total store of contemporary lasing instruments [3]. Various laser approaches worked out and intended for other systems allow improvement of resolution in devices and enhancement of the measurement accuracy. The possibility of employing various contemporary laser technique in overcoming a certain problem depends on parameters of a given device and its compatibility with an object under consideration. Notice that combination of beam methods of dimer generation, laser-based methods of their excitation and standard spectral analysis allows conceptually the study of the dimer ground states for any elements which are found in the solid state under normal conditions.

The analysis of absorption spectra of dimers located inside a low-temperature inert matrix can give some crude information about parameters of free dimers. To this end, an effusion flow of an element under consideration is directed from a Knudsen cell (a thermostat in which an atomic vapor is created) to a crystal of an inert gas or to a gaseous crystal being grown. Atoms and some amount of dimers of this element are trapped in a crystal lattice of the matrix, and the subsequent measurement of the dimer absorption spectrum gives rise to parameters of dimers in the ground state.

These parameters differ from those of free dimers because of dimer interaction with surrounding atoms or molecules in the matrix. As a consequence this approach is useful to the case of strong interaction between identical atoms in the dimer which far exceeds the energy of interaction with surrounding atoms in the matrix crystal lattice. The analysis of measured results for different matrices allows the experimenter to exclude partially the influence of a matrix on dimer parameters. Hence, spectral study of dimers in matrices makes it possible to derive parameters for free dimers.

There are advanced numerical methods of quantum mechanics for calculation of dimer parameters. But now the accuracy and reliability of these methods does not allow them to compete with spectral ones. Nevertheless, the computer methods are progressing rapidly and their possibilities vary. These methods can be applied to dimers of elements with a complex spectrum if generation of dimers demands high temperatures. Or especially in cases when it is difficult to separate spectra for different electronic transitions due to their mixing. Then calculations can give most reliable information on the parameters of dimers or help in interpreting the observed spectra.

5. Spectroscopy of molecules

Among different approaches to the analysis of dimer parameters, the spectral methods fill a central place, and data result from handling of dimer spectra in absorption and emission. Let us consider the peculiarities of radiative transitions in dimers and restrict ourselves to the dipole transitions because in the case of other types of radiative transitions, so-called forbidden transitions, the intensities are by several orders of magnitude weaker than that of the dipole ones. The probability per unit time of a radiative dipole transition is proportional to the square of the matrix element of the dipole moment operator for the electron subsystem [18 – 21]. It allows formulation of the selection rules for dipole radiative transitions in dimers.

Indeed, the operator of the dipole moment equals

$$\mathbf{D} = \sum_j e\,\mathbf{r}_j\,, \tag{7}$$

where e is the electron charge, $\mathbf{r}_j$ is the coordinate of the j-th electron. The operator of electronic dipole moment change its sign under inversion of electrons with respect to the dimer centre. Then the symmetry of the dipole moment operator together with the dimer symmetry lead to the following selection rules at which the matrix element of the dipole moment operator does not equal zero:

$$\mathrm{g} \to \mathrm{u}, \quad \mathrm{u} \to \mathrm{g}; \quad + \to +, \quad - \to -\,. \tag{8}$$

Because the operator of the electron dipole moment can be represented in the form of the spherical harmonic with the unit angular momentum, the following selection rule takes place for the projection of the angular momentum onto the dimer axis:

$$\Delta\Lambda = 0,\ \pm 1. \tag{9}$$

This selection rule is valid for both the Hund's coupling case 'a' (for the projection of the angular electronic momentum) and the Hund's coupling case 'c' (for the projection of the total electronic momentum).

For evaluation of the selection rule in the case of changing the dimer rotational moment, let us represent the dipole moment operator in the form of the spherical harmonic and find its projection onto a fixed axis. Then the probability of the radiative transition between molecular rotational states per unit time is proportional to the square of the following matrix element:

$$\langle JM\,|\,Y_{1m}(\vartheta,\,\varphi)\,|\,J'M'\rangle,$$

where ϑ, φ are the angles characterising the position of the molecular axis in the stationary coordinate system, J, M are the dimer rotational moment and its projection onto a fixed axis in the initial state, J', M' are the same dimer quantum numbers for the final state of the dimer and a given radiative transition, Y_{1m} is the spherical harmonic for the unit angular momentum and its projection m onto the fixed axis. From this formula it follows that the matrix element of the dipole moment operator does not equal zero in the following cases:

$$J' = J,\ J \pm 1. \tag{10}$$

Thus, the radiative spectrum for a given electronic transition constitutes the bands involving spectral lines with different values of J and J'. The band for each electronic transition can include three branches: P-branch with $J' = J + 1$, Q-branch with $J' = J$, and R-branch with $J' = J - 1$. If one of the transition state is characterised by zero projection of the electronic momentum onto the dimer axis, Q-branch is absent in this dimer spectrum.

It follows from the selection rule (8) that the vibrational-rotational transitions for the same electronic term are absent in the case of a dimer whose nuclei make identical isotopes. Notice that for deduction of the selection rules we assumed the electric and geometric dimer centres to be coincident, i.e. dimer nuclei are considered as identical isotopes. If nuclei refer to different isotopes (as, for example, in the molecule HD), the vibrational-rotational radiative transition for the same electronic term is allowed.

The selection rules extract certain electronic terms between which the dipole radiative transitions are possible. Figures 3 – 18 present such radiative transitions for dimers of alkali metals, halogens, some gaseous molecules, mercury, sulfur, helium, and also for the diatomic nitrogen ion. From treatment of the dimer spectra for electronic-vibrational-rotational transitions one can determined parameters of excited diatomic molecules. They are given in Table 4 for some low-excited states of dimers. These spectra allow determination of the behaviour of electronic terms for dimer excited states as a function of the distance between nuclei. These data are presented in Figs 19 – 22 for some gaseous molecules and their ions.

Data of Table 4 lists a part of spectroscopic parameters of dimers. Additional information about radiating states is required for the analysis of these transitions. Indeed, the probability of the radiative transition per unit time $1/\tau$ is proportional to the square of the matrix element of the dipole moment operator so that the expression for this quantity has the form:

$$\frac{1}{\tau} \propto \left| \int \psi_v(R)\,\mu(R)\,\varphi_{v'}(R)\,\mathrm{d}R \right|^2, \tag{11}$$

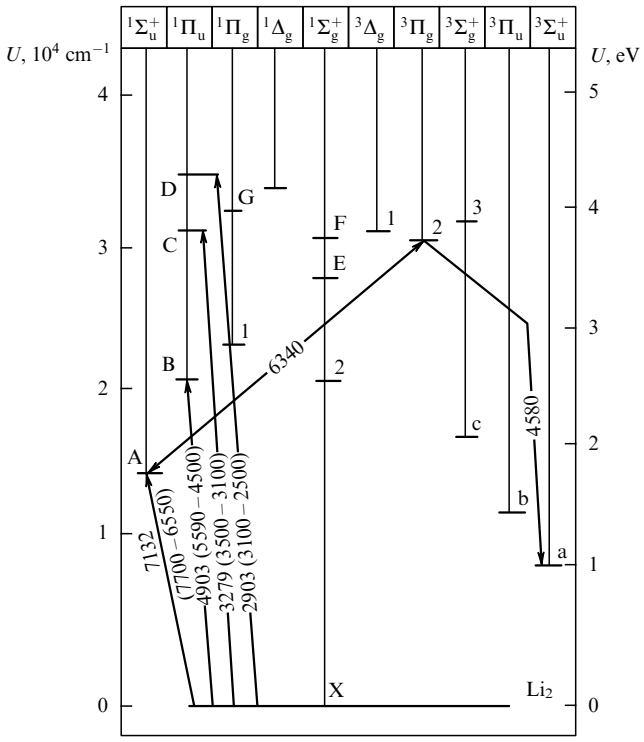

Figure 3. Diagram of allowed transitions between electronic states of the lithium dimer.

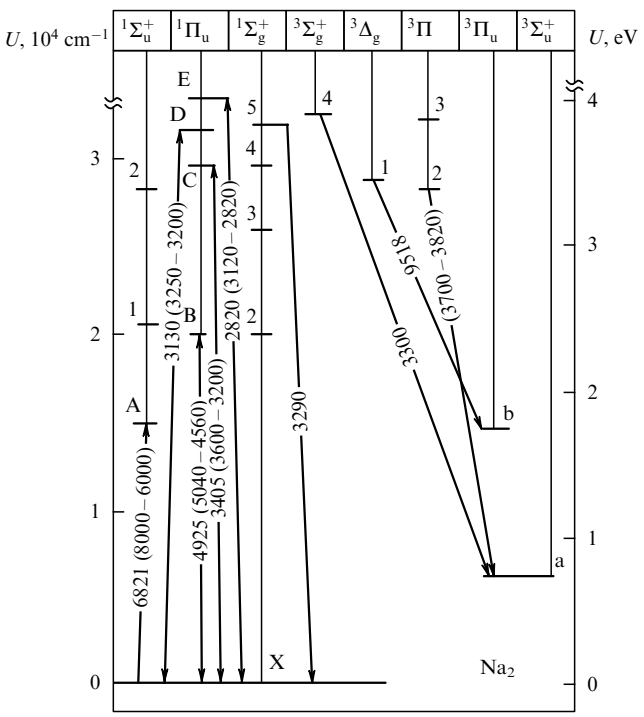

Figure 4. Diagram of allowed transitions between electronic states of the sodium dimer.

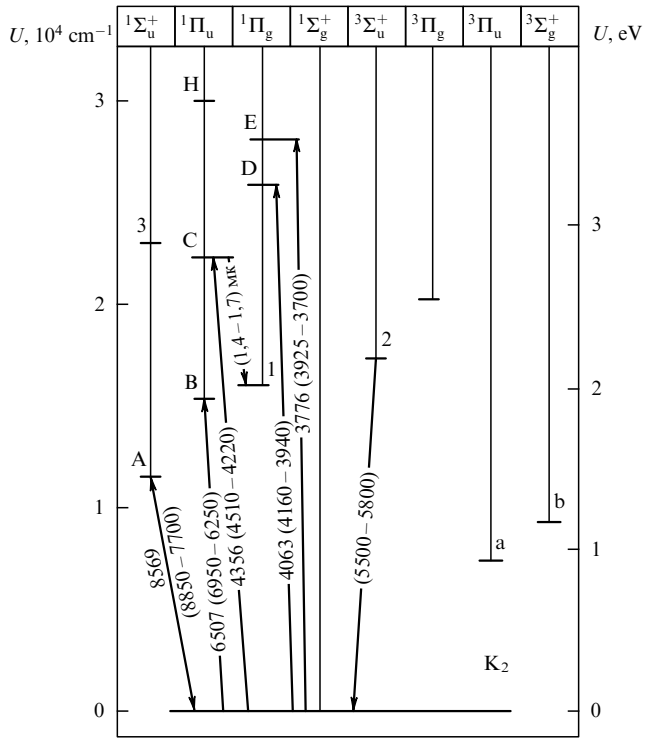

Figure 5. Diagram of allowed transitions between electronic states of the potassium dimer.

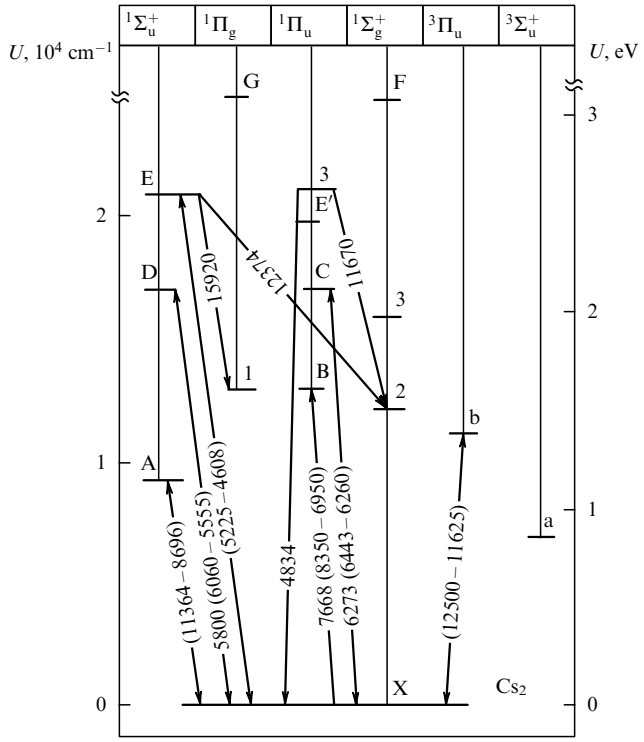

Figure 7. Diagram of allowed transitions between electronic states of the caesium dimer.

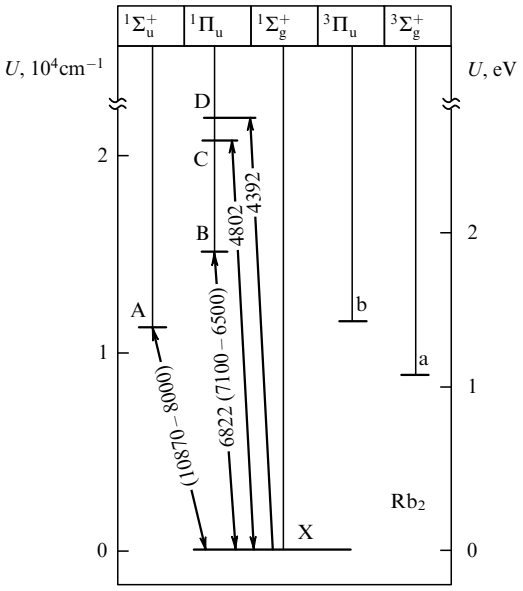

Figure 6. Diagram of allowed transitions between electronic states of the rubidium dimer.

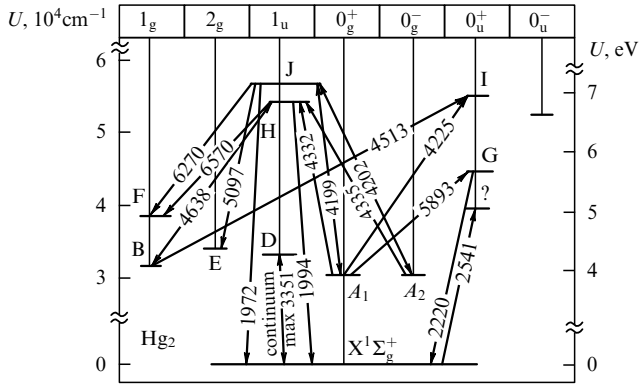

Figure 8. Diagram of allowed transitions between electronic states of the mercury dimer.

where R is the internuclear distance, $\psi_v(R)$, $\varphi_{v'}(R)$ are the wave functions for the vibrational states of the dimer with given values of the vibrational quantum numbers and a certain electronic state, $\mu(R)$ is the matrix element of the dipole moment operator of electrons taken over electronic wave functions of the transition at a given distance between nuclei. If we assume $\mu(R)$ to be independent of the distance between nuclei R, the probability of the radiative transition per unit time is proportional to the square of the integral

$$S_{vv'} = \int \psi_v(R)\, \varphi_{v'}(R)\, \mathrm{d}R\,,$$

which is named the Frank–Condon factor and is determined by overlapping of the vibrational wave functions related to given electronic states. The general problem of determining the Frank-Condon factors and their values for concrete molecules are considered in the monograph [21].

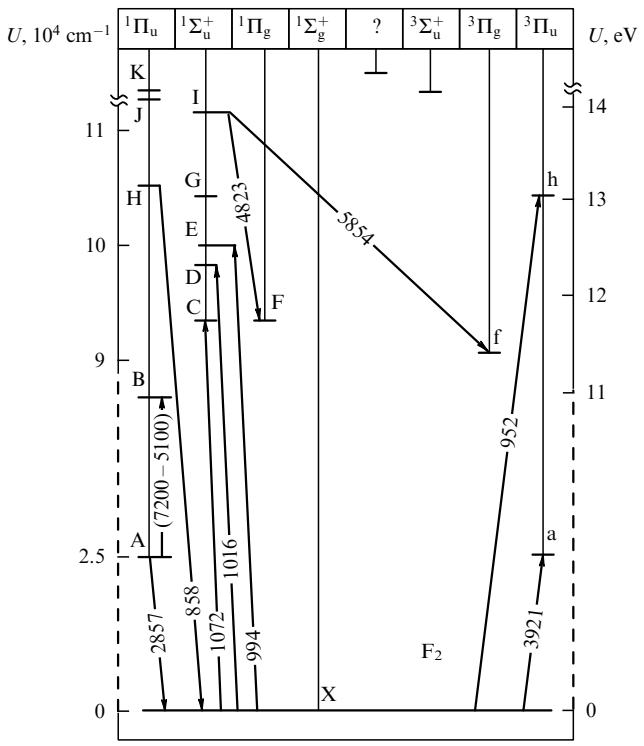

Figure 9. Diagram of allowed transitions between electronic states of the fluorine dimer.

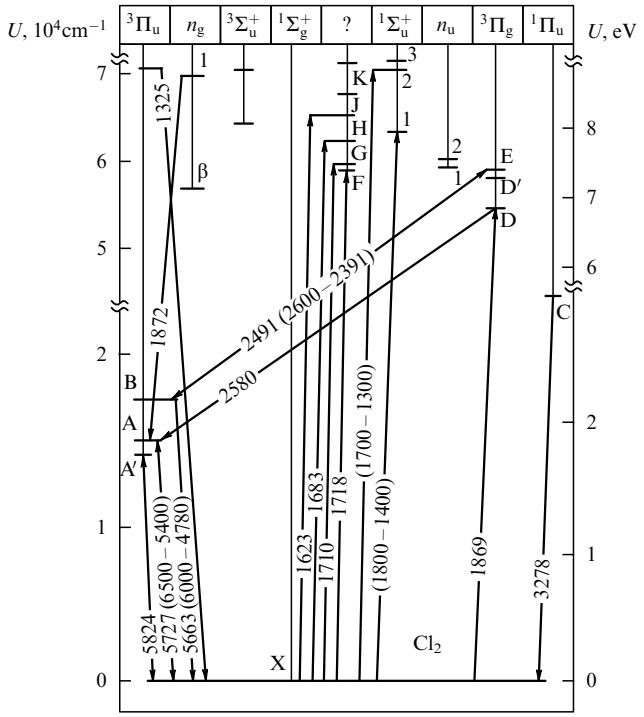

Figure 10. Diagram of allowed transitions between electronic states of the chlorine dimer.

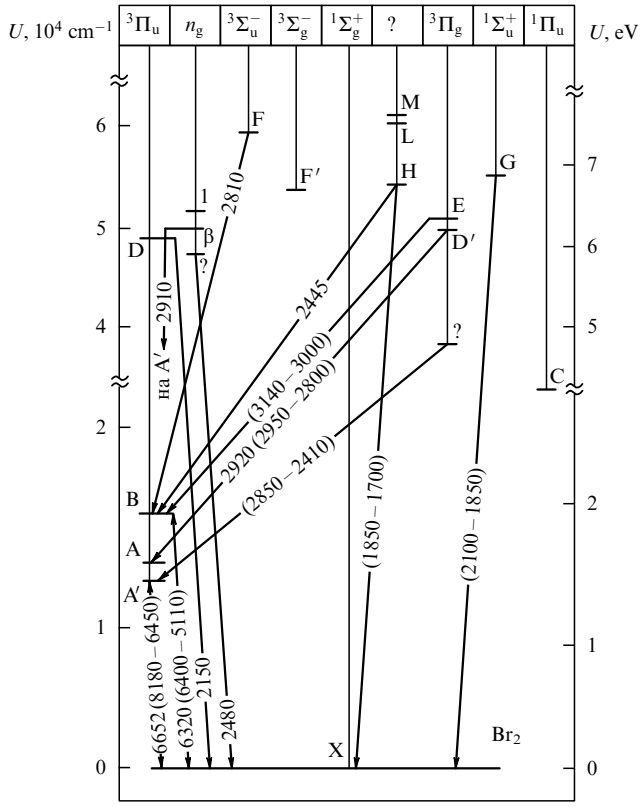

Figure 11. Diagram of allowed transitions between electronic states of the bromine dimer.

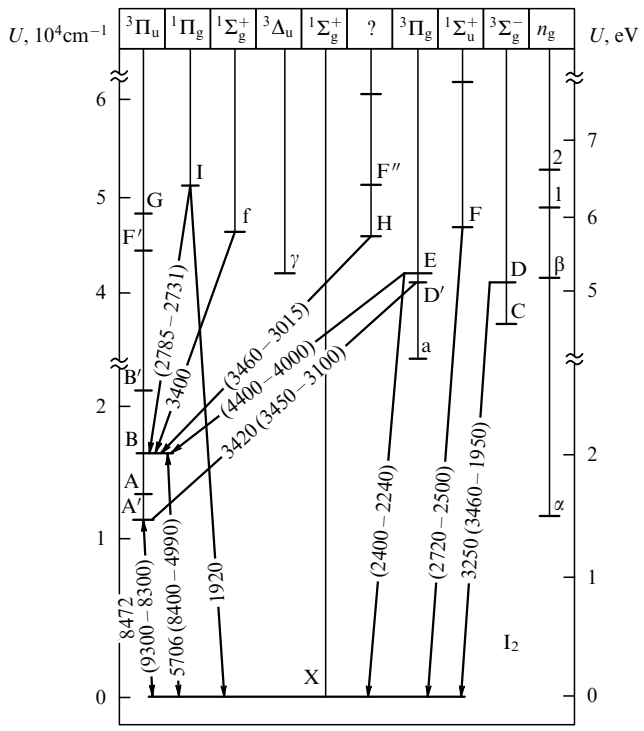

Figure 12. Diagram of allowed transitions between electronic states of the iodine dimer.

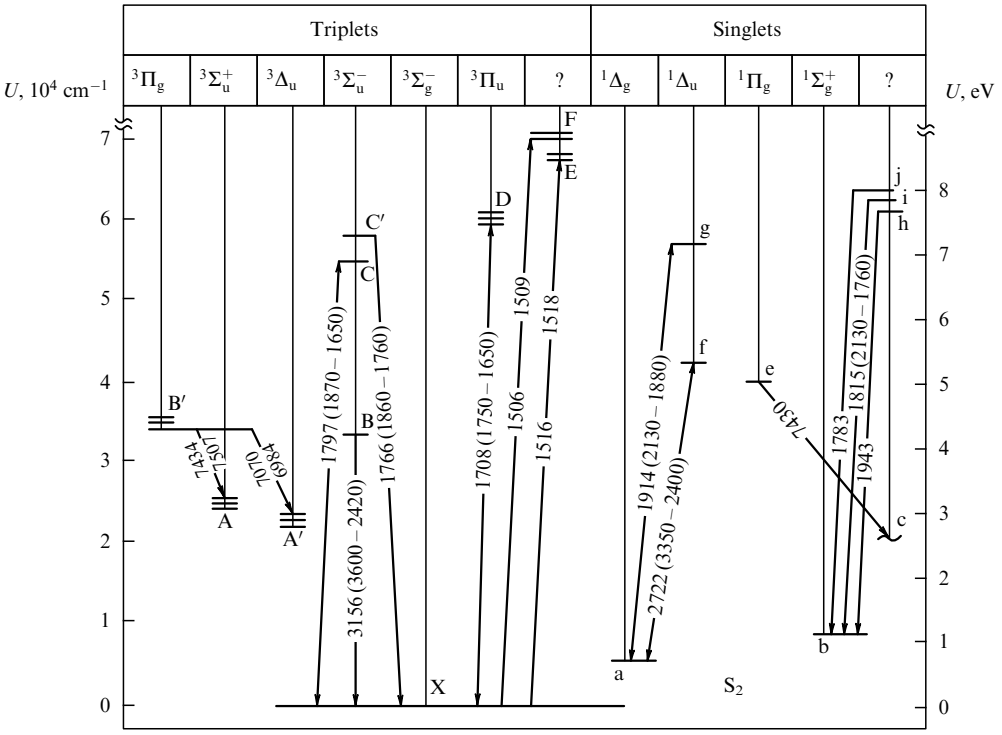

Figure 13. Diagram of allowed transitions between electronic states of the sulfur dimer.

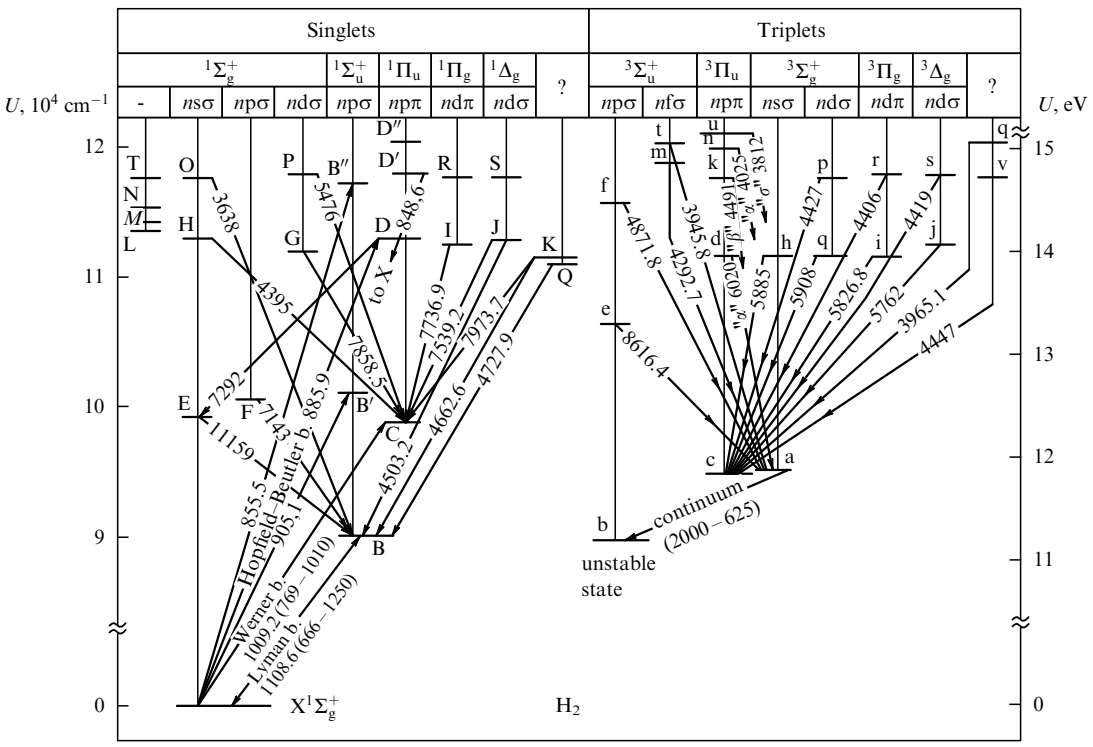

Figure 14. Diagram of allowed transitions between electronic states of the hydrogen dimer.

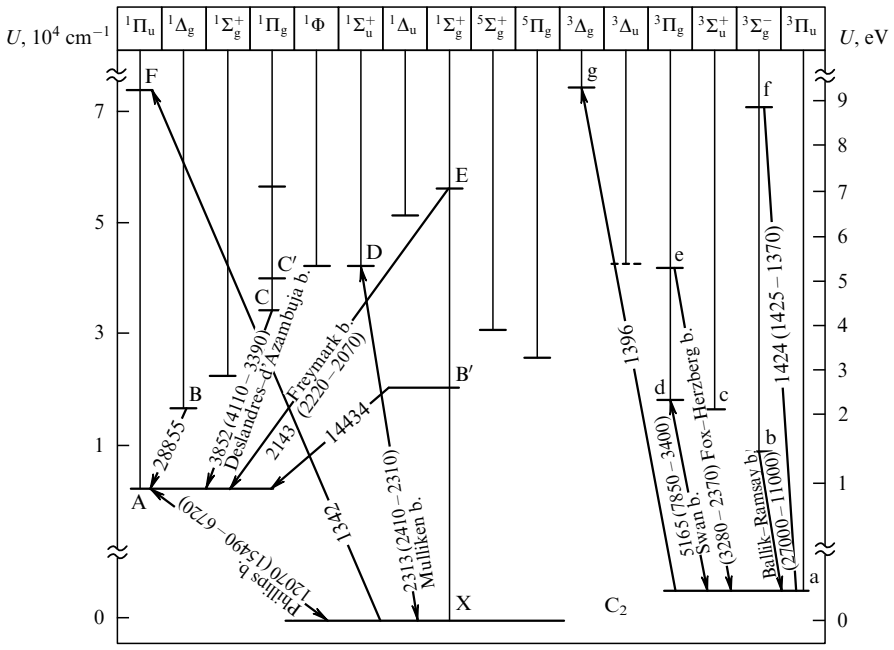

Figure 15. Diagram of allowed transitions between electronic states of the carbon dimer.

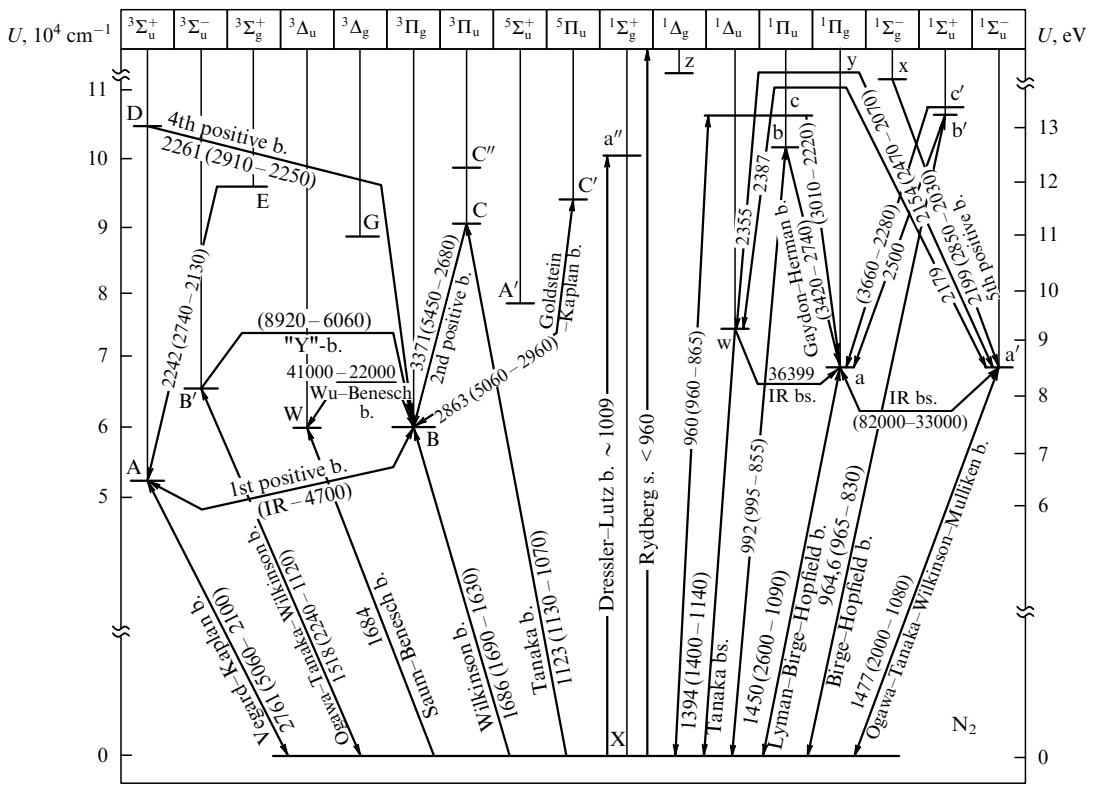

Figure 16. Diagram of allowed transitions between electronic states of the nitrogen dimer.

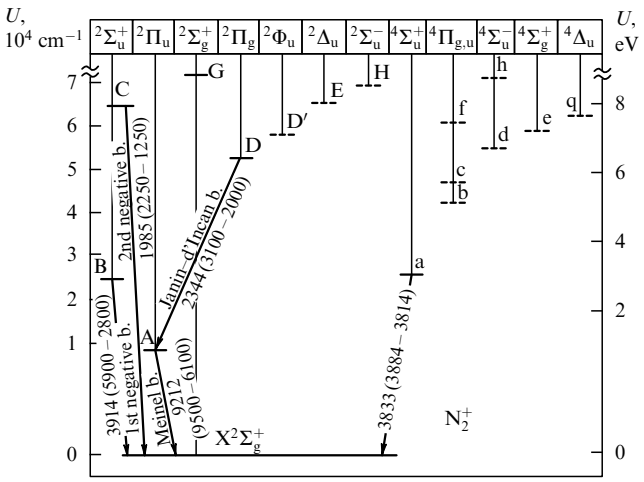

Figure 17. Diagram of allowed transitions between electronic states of the nitrogen diatomic molecular ion.

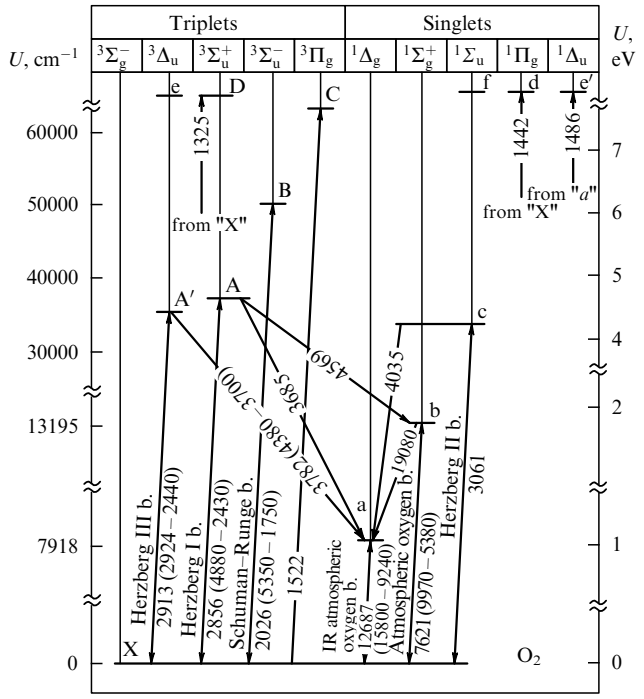

Figure 18. Diagram of allowed transitions between electronic states of the oxygen dimer.

Notice that the function $\mu(R)$ tends to a constant value in the limit of large R, and this constant is not zero if the radiative transition is allowed for states of atoms from which the dimer is formed. When atoms are brought closer together, $\mu(R)$ is generally increased. For dimers of inert gases this function has the maximum at a distance R between nuclei which is compared to the equilibrium internuclear distance in the ground state [22]. This leads to a decrease in the lifetime of the electronically excited diatomic molecule as it suffers vibrational excitation. Table 5 contains the radiative lifetimes of some dimers which are found in the lowest-excited electronic state and in the ground or low-excited vibrational states.

6. Investigation of dimer ions

Spectral studies of positive and negative dimer ions is based on the same procedures as those for neutral dimers. Inasmuch as the concentration of molecular ions in a measuring system is lower than that of diatomics, these methods allow analysis of a small number of excited states in molecular ions. Parameters of the ground-state diatomic molecular ions with identical nuclei are given in Table 6.

A special problem centres around the measurements of ionisation potentials of dimers and their electron affinities which characterise the position of electronic terms in molecular ions with respect to neutral diatomics terms. There is a simple relationship between the ionisation potentials I for the dimer and atom, and the dissociation energies of the dimer and molecular ion, which takes the form

$$I(\mathrm{X}_2) + D(\mathrm{X}_2^+) = D(\mathrm{X}_2) + I(\mathrm{X}), \tag{12}$$

where the symbol in parentheses denotes a particle to which a quantity corresponds. The left hand and right hand sides of this relationship are the energies which are spent on destruction of the dimer into an atom, atomic ion and electron. The similar relationship takes place also for the negative ion of a dimer:

$$EA(\mathrm{X}_2) + D(\mathrm{X}_2) = D(\mathrm{X}_2^-) + EA(\mathrm{X}), \tag{13}$$

where EA is the electron affinity of a particle which is enclosed in parentheses. In this case the left hand and right hand sides of this relationship are the energies which are spent on detachment of electron from the negative dimer ion and formation of two atoms if this process proceeds by two different ways.

The ionisation potential of dimers (see Table 7) can be obtained by the classical analysis of the dimer ionisation by electron impact. Then measurement of the final energy of incident electron, given its initial energy, together with the energy of a released electron allows us to determine the energy which is spent on dimer ionisation, i.e. the ionisation potential of the dimer. This method has drawbacks. First, it gives so-called vertical ionisation potential. Since in the course of electron transitions the nuclei remain stationary, the internuclear distance is conserved under ionisation. If the equilibrium distances between nuclei are different for the dimer and its molecular ion, the vertical ionisation potential differs from its real value, which is defined as the energy of transition from the ground vibrational dimer state to the ground vibrational state of the molecular ion formed. Second, the width of the distribution function for incident electrons is usually several hundredths of eV. Though it can be shortened with a decrease of the electron beam intensity, this fact limits the accuracy of the measured ionisation potential which is estimated for such measurements to be on the order of tenths of eV.

A more precise method of measuring the ionisation potential of dimers is based on the analysis of their Rydberg levels. These levels comprise the bounded states of a molecular ion and highly-excited electron. If these levels are close to the boundary of the continuous spectrum, the difference in energies for neighbouring levels is

Table 4. Spectroscopic parameters of homonuclear diatomic molecules in lower-excited states

Dimer	Term	T_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3} cm^{-1}
Ag_2	$A^1\Sigma_u^+$	22996	154.6	0.59	2.47	0.044	0.219
	$B^1\Pi_u$	35827	151.3	0.70	2.62	0.045	0.249
	$C^1\Pi_u$	37627	172.9	1.1	2.53	0.050	0.268
	$D^1\Sigma_u^+$	39024	168.2	1.1	2.53	0.048	0.282
	$E^1\Pi_u$	40159	146.2	1.6	2.57	0.047	0.416
Al_2	$A'^3\Sigma_g^-$	517	350	2.0	2.48	0.202	1.2
	$a^1\Sigma_g^-$	2547	212	—	2.96	0.143	—
	$b^1\Pi_u$	3343	265	—	2.75	0.165	—
	$c^1\Delta_u$	3503	288	—	2.56	0.191	—
	$d^1\Sigma_g^+$	7182	276	—	2.74	0.167	—
	$B^3\Sigma_u^-$	17120	282	0.83	2.59	0.186	1.3
	$A^3\Sigma_g^+$	17270	350	2.0	2.56	0.191	—
Ar_2	$a^3\Sigma_u^+$	—	298	3.0	2.44	0.142	1.4
	$b^3\Pi_g$	—	295	3.0	2.49	0.136	—
	$A^3\Sigma_u^+$	87458	265	3.1	2.45	0.141	—
	$B^1\Sigma_u^+$	88210	136.5	—	2.82	0.105	—
	$C^3\Pi_u$	95034	68.2	4.6	3.59	0.065	1.8
As_2	$c^3\Sigma_u^+$	14495	315	1.1	2.30	0.817	0.35
	$e^3\Delta_u$	19915	330	0.9	2.35	0.786	—
Au_2	$a^3\Sigma_u^+$	16680	87.8	1.7	2.44	0.027	—
	$A'1_u$	18115	224	3.8	2.40	0.029	—
	$A0_u^+$	19668	143	0.48	2.57	0.025	0.095
	$B'1_u$	24024	127	1.2	2.57	0.025	—
	$B0_g^+$	25686	180	0.68	2.52	0.026	0.096
B_2	$a^5\Sigma_u^-$	1750	1204	9.8	1.54	1.28	11
	$A^3\Pi_u$	3500	818	5.6	1.74	1.006	17
	$1^3\Pi_g$	16497	1130	—	1.48	1.39	—
	$2^3\Pi_g$	22885	1236	8.4	1.63	1.166	3.6
	$3^3\Pi_g$	24558	1288	9.1	1.49	1.37	—
Be_2	$a^3\Sigma_u^+$	4843	517	5.0	2.19	0.783	52
	$b^3\Pi_g$	9557	387	4.2	2.13	0.828	17
	$A'^1\Pi_g$	15985	844	13	2.0	0.936	47
	$A^1\Pi_u$	26265	1093	4.1	1.97	0.963	7.0
	$B^1\Sigma_u^+$	30283	422	15	2.37	0.669	11
Bi_2	$B^3\Sigma_u^+$	5480	134	0.15	2.86	0.018	0.046
	$A^3\Sigma_u^+$	8245	133	0.25	2.86	0.018	—
	$a^3\Delta_u$	9860	125	0.57	2.9	0.018	—
Br_2	$A'^3\Pi_u$	13320	151	2.4	2.68	0.059	0.50
	$A^3\Pi_u$	13905	160	1.6	2.70	0.059	0.49
	$B^3\Pi_u$	15903	168	1.9	2.68	0.059	0.49
C_2	$a^3\Pi_u$	716	1641	12	1.31	1.632	17
	$b^3\Sigma_g^-$	6434	1470	11	1.37	1.499	16
	$A^1\Pi_u$	8391	1608	12	1.32	1.616	17
	$c^3\Sigma_u^+$	9124	2086	19	1.22	1.92	13
	$B^1\Delta_g$	12082	1510	—	1.39	1.45	—
	$B'^1\Sigma_g^+$	15409	1424	—	1.38	1.48	—
	$d^3\Pi_g$	20023	1788	16	1.27	1.74	16
	$C^1\Pi_g$	34261	1809	16	1.26	1.78	18
	$C'^1\Pi_g$	39365	1697	—	1.28	1.72	—
	$e^3\Pi_g$	40797	1107	39	1.54	1.19	24
	$D^1\Sigma_u^+$	43239	1830	14	1.24	1.99	20
	$E^1\Sigma_g^+$	55035	1672	40	1.25	1.79	39
	$1^1\Delta_u$	57720	1150	22	1.44	1.36	26
Ca_2	$a^3\Pi_u$	1170	67.7	—	4.2	0.047	—
	$A^1\Sigma_u^+$	14251	127	0.72	3.63	0.064	—
	$B^1\Sigma_u^+$	18395	137	0.72	3.8	0.058	0.3
Cl_2	$A'^3\Pi_u$	17170	258	4.9	2.43	0.163	1.5
	$A^3\Pi_u$	17460	256	5.1	2.43	0.163	1.5
	$B'^1\Pi_u$	17782	257	5.8	2.43	0.163	1.5

Table 4 (*continued*)

Dimer	Term	T_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3} cm^{-1}
	$B^3\Pi_u$	17809	260	2.7	2.44	0.162	1.5
Cr_2	$A^3\Sigma_u^+$	14240	580	—	1.65	0.24	—
	$B^1\Sigma_u^+$	21753	452	9.0	1.70	0.22	—
Cs_2	$a^3\Sigma_u^+$	3140	50	—	4.3	0.013	—
	$b^3\Pi_u$	7850	—	—	—	—	—
	$A^1\Sigma_u^+$	9627	36.1	0.38	5.29	0.0086	—
	$^3\Sigma_g^+$	11602	—	—	5.54	0.0078	—
	$2^1\Sigma_g^+$	12114	23.4	—	5.83	0.0071	—
	$B^1\Pi_u$	13044	34.3	0.076	4.85	0.0108	—
	$1^1\Pi_g$	13913	18.4	0.078	5.69	0.0074	—
	$C^1\Pi_u$	15948	29.7	0.042	4.54	0.012	0.078
Cu_2	$a^3\Sigma_u^+$	15350	125	—	2.48	0.087	—
	$A^1\Sigma_u^+$	20431	192	0.35	2.28	0.103	1.4
	$B^1\Sigma_u^+$	21758	245	2.0	2.33	0.099	0.61
	$C^1\Pi_u$	21866	221	1.8	2.26	0.105	0.92
Ge_2	$a^3\Pi_u$	767	308	0.5	2.34	0.085	—
H_2	$b^3\Sigma_u^+$	~ 90000	—	—	0.7	68	—
	$B^1\Sigma_u^+$	91700	1358	20.9	1.293	20.02	1293
	$c^3\Pi_u$	95838	2467	63.5	1.038	31.1	1425
	$a^3\Sigma_u^+$	95936	2665	71.6	0.989	34.2	1670
	$E^1\Sigma_g^+$	100082	2589	130	1.012	32.7	1820
	$C^1\Pi_u$	100090	2444	69.5	1.033	31.4	1665
	$e^3\Sigma_u^+$	107775	2196	65.8	1.11	27.3	1510
	$B'^1\Sigma_u^+$	111643	2039.5	83.4	1.119	26.7	2780
	$d^3\Pi_u$	112700	2372	66.3	1.050	30.4	1550
	$i^3\Pi_g$	113130	2253.5	67.0	1.070	29.2	1510
	$I^1\Pi_g$	113140	2259	78.4	1.069	29.3	1580
	$j^3\Delta_g$	113530	2345	66.6	1.054	30.1	1700
	$J^1\Delta_g$	113550	2341	63.2	1.055	30.1	1720
	$D^1\Pi_u$	113877	2364	69.9	1.049	30.4	1680
He_2	$a^3\Sigma_u^+$	144048	1809	38.2	1.05	7.704	228
	$A^1\Sigma_u^+$	146365	1861	35.3	1.04	7.779	217
	$b^3\Pi_g$	148835	1769	35.0	1.06	7.447	220
	$B^1\Pi_g$	149914	1766	34.4	1.07	7.40	220
	$c^3\Sigma_g^+$	155053	1584	52.7	1.09	7.005	310
	$C^1\Sigma_g^+$	157415	1653	41.0	1.09	7.05	210
	$d^3\Sigma_u^+$	164479	1728	36.1	1.07	7.341	224
	$D^1\Sigma_u^+$	165085	1746	35.5	1.07	7.36	218
	$e^3\Pi_g$	165598	1721	35.0	1.08	7.28	221
	$f^3\Sigma_u^+$	165685	1636	44.4	1.09	7.07	250
	$F^1\Sigma_u^+$	165813	1664	40	1.09	7.1	250
	$f^3\Pi_u$	165877	1662	44.8	1.09	7.14	235
	$E^1\Pi_g$	165911	1721	34.8	1.08	7.27	216
	$F^1\Pi_u$	165971	1671	40	1.09	7.16	230
	$f^3\Delta_u$	166303	1707	35.1	1.08	7.23	230
	$F^1\Delta_u$	166304	1707	35.1	1.08	7.23	220
Hg_2	$C1_u$	27570	—	—	2.94	0.03	—
	$A0_g^+$	29000	144	0.4	2.84	0.03	—
	$A0_g^-$	29015	142	0.5	2.84	0.03	—
	$B1_g$	30510	143	—	2.85	0.03	—
	$D1_u$	31942	133	0.52	2.5	0.04	—
	$E2_g$	33191	142	0.5	2.85	0.03	—
I_2	$A'^3\Pi_u$	10042	109	0.81	3.08	0.28	0.3
	$A^3\Pi_u$	10906	92.5	1.2	3.3	0.24	0.1
	$B^3\Pi_u$	15725	126	0.76	3.02	0.29	0.16
K_2	$a^3\Pi_u$	4196	90.0	0.27	3.9	0.057	0.25
	$b^3\Sigma_g^+$	9910	91.9	0.20	3.88	0.057	0.17
	$A^1\Sigma_u^+$	11106	70.9	0.17	4.56	0.042	0.14
	$B^1\Pi_u$	15377	74.9	0.38	4.2	0.049	0.24

Table 4 (*continued*)

Dimer	Term	T_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3} cm^{-1}
	$1^1\Pi_g$	15900	20.0	0.079	6.2	0.022	0.13
	$3^1\Pi_u$	22927	—	—	4.68	0.039	—
	$C^1\Pi_u$	22969	61.5	0.13	4.4	0.044	0.165
Kr_2	$A^3\Sigma_g^+$	74304	245	2.6	2.21	0.081	1.25
	$B^1\Sigma_u^+$	80006	220	2.2	2.43	0.068	0.91
	$C^1\Sigma_u^+$	85520	43.8	1.8	3.7	0.029	0.82
Li_2	$a^3\Sigma_u^+$	8184	65.2	3.3	4.17	0.276	2.4
	$b^3\Pi_u$	11241	346	2.0	2.55	0.717	5.9
	$A^1\Sigma_u^+$	14068	256	1.6	3.11	0.497	5.4
	$1^3\Sigma_g^+$	16329	252	2.4	3.06	0.516	7.6
	$c^3\Sigma_g^+$	16700	240	2.1	3.10	0.501	6.6
	$2^3\Sigma_g^+$	20102	139	2.0	3.65	0.420	1.4
	$B^1\Pi_u$	20436	271	2.9	2.94	0.557	8.3
	$1^1\Pi_g$	21998	93.4	1.9	4.06	0.292	—
N_2	$A^3\Sigma_u^+$	50203	1460	13.8	1.286	1.454	18.0
	$B^3\Pi_g$	59619	1733	14.1	1.212	1.454	17.8
	$W^3\Delta_u$	59808	1501	11.6	1.27	1.5	17.0
	$B'^3\Sigma_u^-$	66272	1517	12.2	1.278	1.473	16.9
	$a'^1\Sigma_u^-$	68152	1530	12.0	1.275	1.479	16.6
	$a^1\Pi_g$	69283	1694	14.0	1.22	1.616	17.9
	$w^1\Delta_u$	72097	1569	11.9	1.268	1.498	16.6
	$A'^5\Sigma_u^+$	77600	850	24.0	1.55	1.00	25.0
	$^1\Sigma_g^+$	85200	1135	6.3	1.64	0.90	6.0
	$G^3\Delta_u$	86800	766	11.9	1.61	0.93	16.1
	$C^3\Pi_u$	89136	2047	28.4	1.148	1.82	18.7
Na_2	$a^3\Sigma_u^+$	5848	152	0.50	3.11	0.152	0.72
	$b^3\Pi_u$	13523	154	0.45	3.42	0.151	0.60
	$A^1\Sigma_u^+$	17541	117	0.36	3.64	0.111	0.55
	$B^1\Pi_u$	20320	124	0.70	3.41	0.125	0.72
Nb_2	A	14649	468	1.4	2.14	0.081	1.4
	B	14845	466	—	2.15	0.081	1.5
O_2	$a^1\Delta_g$	7923	1510	13.06	1.215	1.426	17.2
	$b^1\Sigma_g^+$	13195	1432	13.9	1.226	1.400	18.6
	$c^1\Sigma_u^-$	33057	795.4	12.7	1.518	0.915	13.6
	$A^3\Delta_u$	34757	826.2	16.8	1.526	0.904	16.8
	$A'^3\Sigma_u^-$	35393	799	12.2	1.521	0.910	14.2
	$B'^3\Sigma_g^-$	48792	786.2	10.7	1.91	0.58	5.0
	$B^3\Sigma_u^-$	49005	709.6	10.9	1.604	0.819	12.0
P_2	$a^3\Sigma_u^-$	18798	565	2.75	2.09	0.25	1.5
	$b^3\Pi_g$	28069 28197 28330	645	3.2	1.97	0.28	1.8
	$b'^3\Sigma_u^-$	28503	604	2.0	2.05	0.258	1.4
	$A'^1\Sigma_u^-$	28522	—	—	—	—	—
	$1^5\Sigma_g^+$	31965	393	3.3	2.33	0.202	2.8
	$A^1\Pi_g$	34515	619	3.0	1.99	0.275	1.7
	$C^1\Sigma_u^+$	46941	474	2.3	2.12	0.242	1.8
S_2	$a^1\Delta_g$	4395	702	3.1	1.89	0.293	1.7
	$b^1\Sigma_g^+$	7981	674	3.4	1.91	0.288	1.8
	$c^1\Sigma_u^-$	20203	534	—	2.12	0.235	—
	$A'^3\Delta_u$	20974	488	2.5	1.77	0.228	1.5
	$A^3\Sigma_u^+$	21971	482	2.6	2.16	0.225	1.4
	$B''^3\Pi_u$	30853	336	4.2	2.28	0.203	—
	$B^3\Sigma_u^-$	31689	434	2.8	2.17	0.224	1.8
	$B'^3\Pi_g$	36289	434	2.7	2.08	0.224	—
Sb_2	$X'1_u$	836	259	—	2.58	0.036	11
	$a^3\Sigma_u^+$	9474	206	0.55	—	—	—
	$A^3\Delta_u$	14991	217	0.46	2.64	0.034	—
	$B^3\Sigma_u^-$	19068	219	0.55	2.48	0.039	10

Table 4 (*continued*)

Dimer	Term	T_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r_e, A	B_e, cm^{-1}	α_e, 10^{-3} cm^{-1}
	$K^3\Pi_u$	31397	141	1.1	2.9	0.028	21
	$D^1\Sigma_u^+$	32087	210	—	2.8	0.031	—
Se_2	$X'1_g$	512	387	0.96	2.24	0.90	0.29
	$a'^1\Delta_g$	4000	320	—	2.27	0.90	—
	$b^1\Sigma_g^+$	8557	355	1.1	2.3	0.89	0.32
Si_2	$A^3\Pi_u$	574	448	2.2	2.17	0.256	1.6
	$a^1\Delta_g$	4123	481	5.5	2.33	0.229	1.7
	$b^1\Pi_u$	5395	545	2.8	2.16	0.259	1.3
Sn_2	$X'1_u$	1806	204	0.25	2.63	0.035	—
	$F0_g^+$	17688	83.4	0.035	3.2	0.023	0.26
Sr_2	$A^1\Sigma_u^+$	17358	85.1	0.34	3.95	0.024	—
	$B^1\Pi_u$	22173	80.4	1.8	3.85	0.025	—
Te_2	$X'1_g$	1975	252	0.52	2.56	0.0405	0.10
	$a^1\Delta_g$	6500	235	—	2.7	0.036	—
	$b^1\Sigma_g^+$	9600	229	0.60	2.59	0.039	0.11
Xe_2	$A1_u$	63089	137	1.2	3.01	0.028	—
	$B0_u^+$	63796	125	0.94	3.02	0.028	—
	$B'1_u$	68200	5,9	0.17	5.46	0.009	—
Zr_2	$A^1\Sigma_u^+$	11508	214	—	2.8	0.047	—
	$B^1\Pi_u$	17120	260	—	2.4	0.025	—
	$C^3\Pi_u$	18615	243	—	2.5	0.059	—
	$D^1\Sigma_u^+$	22916	354	—	2.6	0.055	—

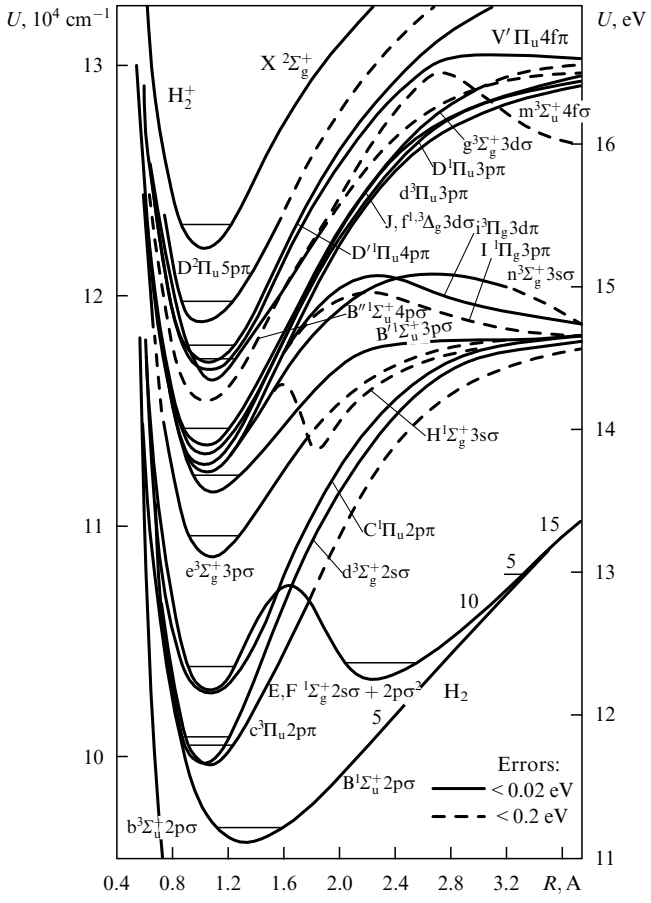

Figure 19. Potential curves for interaction of two hydrogen atoms or a proton and hydrogen atom.

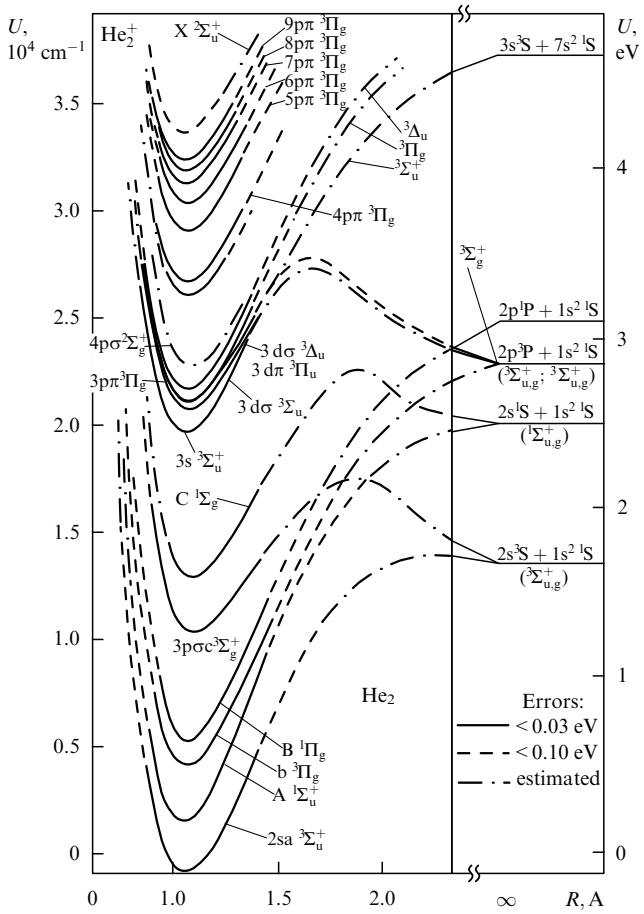

Figure 20. Potential curves for interaction of two helium atoms.

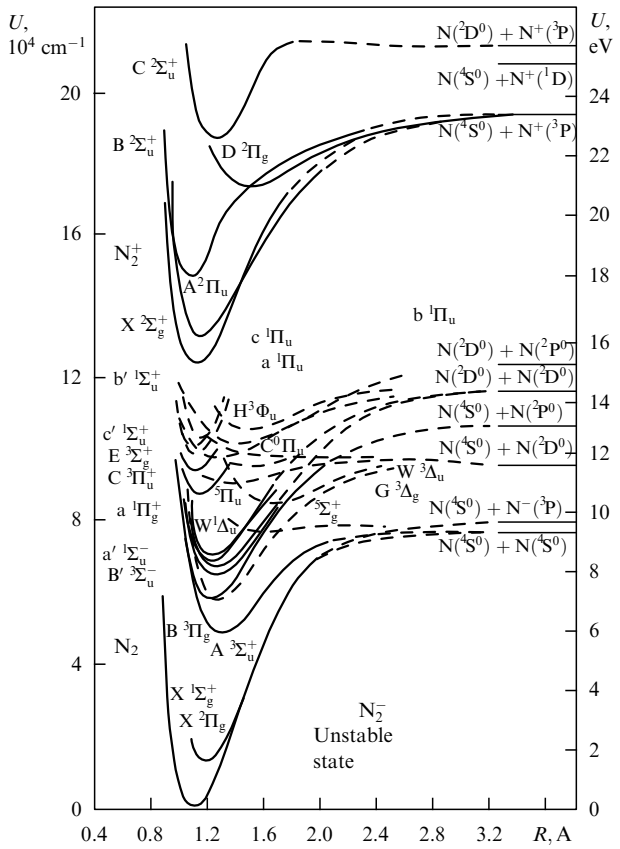

Figure 21. Electronic terms for a nitrogen dimer and its molecular ion.

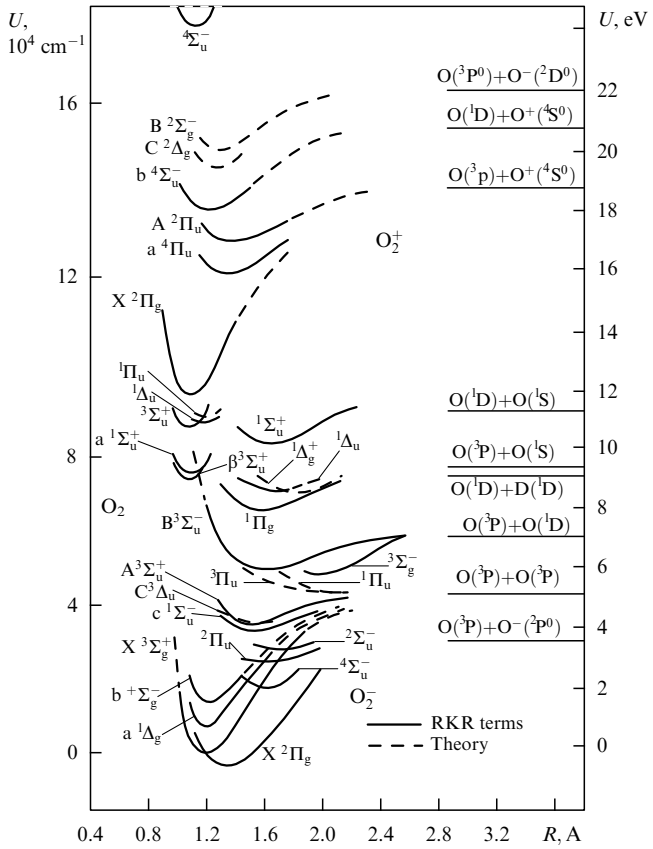

Figure 22. Electronic terms for an oxygen dimer and its molecular ion.

Table 5. Radiative lifetimes τ for lower-excited electronic states of dimers in the ground vibrational state

Dimer	Ground state term	Lower-excited state		τ, ns
		Term	T_e, cm^{-1}	
As_2	$X\,^1\Sigma_g^+$	$c^3\Sigma_u^+$	14495	1.2×10^4
Au_2	$X\,^1\Sigma_g^+$	$a^3\Sigma_u^+$	16680	75
Br_2	$X\,^1\Sigma_g^+$	$A'^3\Pi_u$	13320	4×10^3
Cd_2	$X\,^1\Sigma_g^+$	$A0_u^+$	30910	840
H_2	$X\,^1\Sigma_g^+$	$B^1\Sigma_u^+$	91700	3.5
N_2	$X\,^1\Sigma_g^+$	$A^3\Sigma_u^+$	50203	2×10^9
O_2	$X\,^3\Sigma_g^-$	$c^1\Delta_g$	7923	3×10^{12}
Ti_2	$X\,^3\Delta_g$	$^3\Pi_u$	10480	5×10^3
Xe_2	$X\,^1\Sigma_g^+$	$A1_u$	63089	170

$2\mathrm{Ry}/(n-\delta)^3$, where Ry = 13.605 eV is the Rydberg constant expressed in corresponding units, δ is the quantum defect for this group of levels. Comparison of transition energies for several highly-excited states from this group allows determination both the dimer ionisation potential and the quantum defect of these states. The accuracy of measuring the ionisation potential is better in the best cases than one thousandths of eV.

The most precise determination of dimer electron affinities concerns the method of photoelectron spectroscopy and has the same form as in the atomic case. Indeed, a beam of atoms and molecules with an admixture of negative ions is crossed by a laser beam. An interaction with the laser photons can lead to detachment of electrons from the negative ions. Then two methods of measuring the electron binding energy in the negative ion are used. In the first case, the photon energy is fixed and the energy of released electron is measured at a certain angle to the beam. The difference between photon and electron energies gives the electron binding energy in the negative ion. In the second method, the photon energy is tuned and the dependence of the flux intensity of released electrons versus the photon wavelength is found. The threshold for this process deduced by approximating the measured dependence gives the electron affinity of dimers. Naturally, the approximation of a measured signal close to the threshold must take into account the near-threshold dependence of the photodetachment cross section for the negative ion. These methods allow determination of the electron affinities of dimers (see Table 7) with a high accuracy.

7. Conclusions

By this means the revision of data for parameters of dimers and methods of their determination shows that a remarkable progress was reached in the last decade for investigation of metal dimers due to beam techniques of dimer generation, excitation and detection. In other cases, a slow improvement of the data accuracy and authenticity is observed using the traditional methods and approaches.

Table 6. Spectroscopic parameters of molecular ions of dimers in the ground state

Ion	Term	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	r, A	B_e, cm^{-1}
Ag_2^+	$X^2\Sigma_g^+$	118	0.05	2.8	0.040
Ag_2^-	$X^2\Sigma_u^+$	145	0.9	2.6	0.046
Al_2^+	$X^2\Sigma_g^+$	178	2.0	3.2	0.122
Al_2^-	$X^4\Sigma_g^-$	335	—	2.65	0.178
Ar_2^+	$X^2\Sigma_u^+$	308.9	1.66	2.43	0.143
As_2^+	$X^2\Sigma_g^+$	430	—	1.9	0.125
B_2^+	$X^2\Sigma_g^+$	357	—	4.15	0.181
Be_2^+	$X^2\Sigma_u^+$	502	4.2	2.23	0.752
Be_2^-	$X^2\Sigma_g^+$	620	—	2.3	—
Bi_2^+	$X^2\Pi_g$	143.4	0.18	—	—
Bi_2^-	$X^2\Pi_g$	152	0.53	2.83	0.020
Br_2^+	$X^2\Pi_g$	376	1.13	2.3	0.088
Br_2^-	$X^2\Sigma_u^+$	178	0.88	2.81	0.054
C_2^+	$X^4\Sigma_g^-$	1351	12.1	1.41	1.41
C_2^-	$X^2\Sigma_g^+$	1781	11.7	1.27	1.746
Ca_2^+	$X^2\Sigma_u^+$	119	—	3.7	0.053
Cl_2^+	$X^2\Pi_g$	645.6	3.02	1.88	0.265
Cl_2^-	$X^2\Sigma_u^+$	277	1.8	—	—
Cs_2^+	$X^2\Sigma_g^+$	32.4	0.051	4.44	0.013
Cs_2^-	$X^2\Sigma_u^+$	28.4	0.042	4.8	0.011
Cu_2^+	$X^2\Sigma_g^+$	188	0.75	2.35	0.096
Cu_2^-	$X^2\Sigma_u^+$	196	0.7	2.34	0.097
F_2^+	$X^2\Pi_g$	1073	9.13	1.32	1.015
F_2^-	$X^2\Sigma_g^+$	475	5.1	1.92	0.47
Ga_2^+	$X^2\Sigma_g^+$	108	—	3.24	0.046
Ga_2^-	$X^4\Sigma_g^-$	197	—	2.56	0.074
Ge_2^+	$X^4\Sigma_g^-$	256	—	2.32	0.086
H_2^+	$X^2\Sigma_g^+$	2323	67.5	1.06	30.21
He_2^+	$X^2\Sigma_g^+$	1698.5	35.3	1.08	7.21
Hg_2^+	$X^2\Sigma_u^+$	91.6	0.301	2.8	0.021
I_2^+	$X^2\Pi_g$	243	—	2.58	0.040
K_2^+	$X^2\Sigma_g^+$	73.4	0.2	4.6	0.042
Kr_2^+	$X^2\Sigma_u^+$	178	0.82	2.8	0.051
Li_2^+	$X^2\Sigma_g^+$	263.1	1.61	3.12	0.49
Li_2^-	$X^2\Sigma_u^+$	233.1	1.92	2.8	0.516
N_2^+	$X^2\Sigma_g^+$	2207	16.2	1.12	1.932
Na_2^+	$X^2\Sigma_g^+$	120.8	0.46	3.54	0.113
Ne_2^+	$X^2\Sigma_u^+$	586	5.4	1.75	0.554
Ni_2^+	$X^4\Sigma_u^-$	180	—	1.97	0.148
O_2^+	$X^2\Pi_g$	1905	16.3	1.12	1.689
O_2^-	$X^2\Pi_g$	1090	10	1.35	1.12
P_2^+	$X^2\Pi_u$	672	2.74	1.98	0.276
P_2^-	$X^2\Pi_g$	640	—	1.98	0.277
Pb_2^-	$X^2\Pi_g$	129	0.2	2.81	0.021
Rb_2^+	$X^2\Sigma_g^+$	44.5	—	4.8	0.017
Rb_2^-	$X^2\Sigma_u^+$	28.3	—	4.8	0,017
S_2^+	$X^2\Pi_u$	806	3.33	1.82	0.318
S_2^-	$X^2\Pi_u$	601	2.16	1.8	0.32
Se_2^+	$X^2\Pi_u^+$	450	—	2.07	0.10
Se_2^-	$X^2\Pi_g$	330	0.86	—	—
Si_2^+	$X^2\Pi_u$	528	—	2.19	0.25
Sn_2^-	$X^2\Pi_g$	200	0.7	2.66	0.040
Sr_2^+	$X^2\Sigma_u^+$	86	0.54	3.9	0.025
Xe_2^+	$X^2\Sigma_g^+$	123	0.63	3.25	0.026

Table 7. Energy parameters of dimer molecular ions. (The dimer ionisation potential $I(X_2)$, the dissociation energy of the positive $D_0(X_2^+)$ and negative $D_0(X_2^-)$ molecular ions, the electron affinity of the dimer $EA(X_2)$ are depicted.)

X_2	$I(X_2)$, eV	$D_0(X_2^+)$, eV	$D_0(X_2^-)$, eV	$EA(X_2)$, eV
Ag_2	7.66	1.69	1.37	1.03
Al_2*	4.84	1.4	2.4	1.1
Ar_2	14.5	1.23	no	no
As_2	9.64	4.11	2.7	0.1
At_2	8.3	2.4	—	—
Au_2*	9.2	0.02	1.9	1.94
B_2*	8.8	1.9	4.2	1.7
Be_2	7.45	1.9	2.8	0.4
Bi_2	7.44	1.89	2.8	1.27
Br_2	10.52	2.96	1.2	2.55
C_2	12.15	5.3	8.5	3.27
Ca_2	5.2	1.04	—	—
Cl_2	11.50	3.95	1.26	2.38
Co_2	6.0	2.75	1.35	1.11
Cr_2	6.8	1.8	0.17	—
Cs_2	3.76	0.61	0.45	0.47
Cu_2	7.90	1.8	1.57	0.84
D_2	15.467	2.692	—	—
F_2	15.47	3.34	1.3	3.08
Fe_2	6.3	2.7	1.6	0.90
Ga_2*	6.5	1.27	2.1	1.2
Ge_2*	7.2	2.91	—	—
H_2	15.426	2.650	—	—
He_2	22.22	2.47	2.06	—
Hg_2	9.4	0.96	—	—
I_2*	9.3	1.92	1.05	2.55
K_2	4.06	0.81	—	0.49
Kr_2	12.97	1.15	—	no
Li_2	5.14	1.28	0.88	0.7
Mg_2*	6.7	1.3	—	—
Mo_2	6.2	5.0	—	—
Mn_2	6.47	1.3	—	—
N_2	15.581	8.713	—	no
Na_2	4.9	0.98	0.44	0.43
Nb_2	6.37	5.87	—	—
Ne_2	20.4	1.2	—	—
Ni_2	7.43	2.35	1.81	0.93
O_2	12.07	6.66	4.16	0.45
P_2	10.56	5.0	4.8	0.59
Pb_2	6.1	1.7	1.37	1.66
Pt_2	8.7	3.26	2.91	1.9
Rb_2	3.9?	0.75	0.5	0.50
Re_2	—	—	—	1.57 [228]
S_2	9.4	5.4	3.95	1.67
Sb_2	8.7	3.2	—	—
Se_2	8.9	4.4	—	1.94
Si_2	7.4	3.24	3.3 [247]	2.19 [246]
Sn_2	7.38	1.96	—	—
Sr_2	4.74	1.1	—	—
Te_2	8.2	3.5	—	1.92
Ti_2	6.0	2.44	—	—
V_2	6.36	3.14	—	—
Zn_2	9.0	0.42	—	—

* All values are in eV.

References

1. Huber K P, Herzberg G *Molecular Spectra and Molecular Structure. IV Constants of Diatomic Molecules* (New York: Van Nostrand, 1945)
2. Smirnov B M, Yatsenko A S *Reviews of Plasma Chemistry* (Ed. B M Smirnov) (New York: Consultant Bureau, 1991–1994) Vol. 1, p. 31; Vol. 2, p. 103
3. Demtröder W Laser Spectroscopy, 2nd ed. (Berlin, Heidelberg: Springer–Verlag, 1982)
4. Landau L D, Lifshitz E M *Quantum Mechanics* (Adddison-Wesley, Reading, Mass., 1958)
5. Hund F *Z. Phys.* **36** (9–10) 657 (1926)
6. Mulliken R S *Rev. Mod. Phys.* **2** 60 (1930)
7. Wigner E, Witmer E E *Z. Phys.* **51** 859 (1928)
8. Mulliken R S *Rev. Mod. Phys.* **4** 1 (1932)
9. Galitskiĭ V M, Nikitin E E, Smirnov B M *Theory of Collisions of Atomic Particles* (Moscow: Nauka, 1981) (in Russian)
10. Birge R T, Sponer H *Phys. Rev.* **28** 259 (1926)
11. Pearse R W B, Gaidon A G *The Identification of Molecular Spectra* (London: Chapmen and Hall, 1941)
12. Aziz R A, Slaman M J *J. Chem. Phys.* **130** 187 (1989)
13. Aziz R A, Slaman M J *J. Chem. Phys.* **92** 1030 (1990)
14. Dham A K, Allnatt A R, Meath W J, Aziz R A *Mol. Phys.* **67** 1291 (1989)
15. Dham A K et al. *Chem. Phys.* **142** 173 (1990)
16. Beutel V et al. *J. Chem. Phys.* **98** 2699 (1993)
17. Powers D E et al. *J. Chem. Phys.* **78** 2886 (1983)
18. Haitler W *The Quantum Theory of Radiation, 3rd ed.* (Oxford: Oxford University Press, 1954)
19. Sobelman I I *Atomic Spectra and Radiative Transitions* (Berlin: Springer, 1979)
20. Krainov V P, Reiss H, Smirnov B M *Radiative Processes in Atomic Physics* (New York: Wiley, 1996)
21. Kuznetsova L A et al. *Probabilities of Optical Transitions in Diatomic Molecules* (Moscow: Nauka, 1980) (in Russian)
22. Madej A A, Stoicheff B P *Phys. Rev. A* **38** 3456 (1988)
23. Kleman H, Lindkvist St *Ark. Fys.* **9** 385 (1954)
24. Brown C M, Ginter M L *J. Mol. Spectrosc.* **69** 25 (1978)
25. Simard B et al. *Chem. Phys. Lett.* **186** 415 (1991)
26. Saito Y *Jpn. J. Appl. Phys.* **28** 2024 (1989) part 2
27. Cai M et al. *Chem. Phys.* **155** 233 (1991)
28. Zhenwen F et al. *J. Chem. Phys.* **93** 8420 (1990)
29. Sunil K, Jordan K *J. Phys. Chem.* **92** 2774 (1988)
30. Kane D et al. *J. Chem. Phys.* **96** 6407 (1992)
31. Cachoncinlle G et al. *J. Chem. Phys.* **96** 6093 (1992)
32. Conrad N et al. *Z. Phys. D* **16** 71 (1990)
33. Herman P, Madej A, Stoicheff B *Chem. Phys. Lett.* **134** 209 (1987)
34. Herring C et al. *J. Chem. Phys.* **101** 4561 (1994)
35. Balasubramanian K *J. Mol. Spectrosc.* **121** 465 (1987)
36. Yoo R K, Rascis B, Berkowitz J *J. Chem. Phys.* **96** 6696 (1992)
37. Bisher G, Morse M *J. Chem. Phys.* **95** 5646 (1991)
38. Simard B, Hackett P *J. Mol. Spectrosc.* **142** 310 (1990)
39. Das K, Balasubramanian K *J. Mol. Spectrosc.* **140** 280 (1990)
40. Brazier C R, Carrick P *J. Chem. Phys.* **96** 8684 (1992); **100** 7928 (1994)
41. Hachey M, Karna S, Grein F *J. Phys. B* **25** 1119 (1992)
42. Bruna P J, Wright J S *J. Phys. B* **23** 2197S (1990)
43. Clements R, Barrow R *J. Chem. Soc. Faraday Trans.* **81** 625 (1985)
44. Xi L et al. *Acta Opt. Sin.* **9** 140 (1989)
45. Hugreve H *Chem. Phys. Lett.* **187** 479 (1991)
46. Fisher I et al. *Chem. Phys.* **151** 295 (1991)
47. Meng B, Bruna P, Wright J *J. Mol. Phys.* **79** 1305 (1993)
48. Glownia J, Misewich J, Sorokin P *J. Chem. Phys.* **92** 3335 (1990)
49. Balasubramanian K, Liao D *J. Chem. Phys.* **95** 3064 (1991)
50. Polak M et al. *J. Chem. Phys.* **95** 3053 (1991)
51. Barrow R et al. *J. Mol. Spectrosc.* **51** 428 (1974)
52. Brand J et al. *J. Mol. Spectrosc.* **123** 84 (1987)
53. Balasubramanian K *Chem. Phys.* **119** 41 (1988)
54. Koenders B et al. *Chem. Phys. Lett.* **147** 310 (1988)
55. Lawler K et al. *Chem. Phys. Lett.* **168** 168 (1990)
56. Martinez F et al. *J. Phys. B* **24** 2765 (1991)
57. Ishiwata T et al. *J. Mol. Spectrosc.* **151** 513 (1992)
58. Zackrisson M *J. Mol. Spectrosc.* **163** 371 (1994)
59. Xu L et al. *J. Chem. Phys.* **101** 3524 (1994)
60. Douay M, Nietmann R, Bernath P *J. Mol. Spectrosc.* **131** 250, 261 (1988)
61. Maier J, Rösslein M *J. Chem. Phys.* **88** 4614 (1988)
62. Sasada H et al. *J. Chem. Phys.* **94** 2401 (1991)
63. Prasad C, Bernath P *Astrophys. J.* **426** 812 (1994)
64. Hofmann R, Harris D *J. Chem. Phys.* **85** 3749 (1986)
65. Czajkowski M, Bobkowski R, Krause L *Phys. Rev. A* **40** 4338 (1989)
66. Rodriguez G, Eden J *J. Chem. Phys.* **95** 5539 (1991)
67. Wörmer J et al. *Chem. Phys. Lett.* **170** 419 (1990)
68. Koenders B et al. *J. Chem. Phys.* **91** 6042 (1989)
69. Tellinghuisen P et al. *J. Mol. Spectrosc.* **128** 268 (1988)
70. Li Li et al. *J. Chem. Phys.* **88** 4608 (1988)
71. Zattropulos V et al. *Chem. Phys. Lett.* **179** 258 (1991)
72. Ivanov V S, Sovkov V B *Optics Spektroskopy* **70** 28 (1991)
73. Olmo A et al. *J. Mol. Spectrosc.* **145** 323 (1991)
74. Ishiwata T, Kasai Y, Obi K *J. Chem. Phys.* **95** 60 (1991); **96** 5678 (1992)
75. Choi J, Hardwick J *J. Mol. Spectrosc.* **137** 138 (1989)
76. Bramle S, Hamilton P *J. Chem. Soc. Faraday Trans.* **86** 2009 (1990)
77. Sappey A, Harrington J, Weisshaar J *J. Chem. Phys.* **91** 3854 (1989)
78. Sappey A, Harrington J, Weisshaar J *Chem. Phys. Lett.* **204** 235 (1992)
79. Scuseria G, Schaefer H *Chem. Phys. Lett.* **171** 501 (1990)
80. Lessen D, Asher R, Brucat P *Chem. Phys. Lett.* **182** 412 (1991)
81. Casey S, Leopold D *J. Phys. Chem.* **97** 816 (1993)
82. Amiot C, Demtröder W, Vidal C *J. Chem. Phys.* **88** 5265 (1988); **89** 3993 (1988)
83. Yokoyama K, Baba M, Kato H *J. Chem. Phys.* **89** 1209 (1988)
84. Bhale G, Sasso A, Demtröder W *Chem. Phys. Lett.* **188** 376 (1992)
85. Smirnov A D *Z. Prikl. Spektros.* **59** 479 (1993)
86. Suemitsu H, Kitaura H, Seki K *J. Phys. Soc. Jpn.* **62** 3425 (1993)
87. Kim B, Yoshinara K *Phys. Rev. Lett.* **73** 424 (1994)
88. Sappey A et al. *J. Chem. Phys.* **88** 5243 (1988); **91** 3854 (1989)
89. McCaffrey J et al. *J. Chem. Phys.* **91** 92 (1989)
90. Page R H, Gudeman C *J. Chem. Phys.* **94** 35 (1991)
91. Sappey A, Gemble T, Harrington J *J. Appl. Phys.* **53** 353 (1992)
92. Ram R, Jarman C, Bernath P *J. Mol. Spectrosc.* **155** 315 (1992)
93. Chutjian A, Alajajian S *Phys. Rev. A* **35** 4512 (1987)
94. Gordon M, Truhlar D *Theor. Chim. Acta* **71** 1 (1987)
95. Sakai T et al. *J. Phys. B* **21** 229 (1988)
96. Watts J, Bartlett R *J. Chem. Phys.* **95** 6652 (1991)
97. Dhar S, Kestner N *Phys. Rev. A* **38** 1111 (1988)
98. Leopold D G et al. *J. Chem. Phys.* **88** 3780 (1988)
99. Mutsumi T, Hiroshi T *J. Chem. Phys.* **88** 1828 (1988)
100. Baranov S V, Sankevich P A, Sulakshin S S *High Temperatures* **27** 821 (1989)
101. Shim I, Mandik K, Gingerich K *J. Phys. Chem.* **95** 5435 (1991)
102. Balasubramanian K *J. Phys. Chem.* **94** 7764 (1990)
103. Balasubramanian K *J. Mol. Spectrosc.* **123** 228 (1987)
104. Andzelm J, Russo N, Salahub D R *J. Chem. Phys.* **87** 6562 (1987)
105. Bruna P, Grein F *Mol. Phys.* **74** 1133 (1991)
106. Kwok T, Dalgarno A, Rosen A *Phys. Rev. A* **32** 646 (1985)
107. Wallace L, Glab L, Hessler J *Phys. Rev. A* **35** 2102 (1987)
108. Guberman S, Dalgarno A *Phys. Rev. A* **45** 2784 (1992)
109. Ajello J, Shemansky D *Astrophys. J.* **407** 820 (1993)
110. Basterrechea F et al. *Mol. Phys.* **81** 1435 (1994)
111. Freund R, Shiavone J, Crosswhite H *J. Phys. Chem. Ref. Data* **14** 235 (1985)
112. Pratt S, Dehmer P, Dehmer J *J. Chem. Phys.* **92** 262 (1990)
113. Jungen C, Dabrowski I, Herzberg G, Vervloet M *J. Mol. Spectrosc.* **153** 11 (1992)
114. Knowles P et al. *Mol. Phys.* **85** 243 (1995)
115. Hill P *Phys. Rev. A* **40** 5006 (1989)
116. Ginter D, Ginter M *J. Mol. Spectrosc.* **138** 29 (1989)
117. Yarkony D *J. Chem. Phys.* **90** 7164 (1989)
118. Schlauf M et al. *J. Chem. Phys.* **90** 4630 (1989)
119. Balasubramanian K, Das K, Liao D *Chem. Phys. Lett.* **195** 487 (1992)
120. Koperski J, Atkinson J, Krause L *Can. J. Phys.* **72** 1070 (1994)
121. Donovan R et al. *Chem. Phys. Lett.* **122** 612 (1985)
122. Hoy A, Jaywant S, Brand J *Mol. Phys.* **60** 749(1987)

123. Mason S, Tuckett R *Chem. Phys. Lett.* **160** 575 (1989)
124. Li J, Balasubramanian K *J. Mol. Spectrosc.* **138** 162 (1989)
125. Lipson R H, Hoy A, McDonald N *Chem. Phys. Lett.* **168** 25 (1990)
126. Lipson R H, Hoy A, McDonald N *Chem. Phys.* **140** 187 (1990)
127. Gerstnkorn S, Luc P, Le Roy R *Can. J. Phys.* **69** 1299 (1991)
128. Suwaiyan A, Mastomarino J, Klein U *Chem. Phys. Lett.* **192** 581 (1992)
129. Golikova E V et al. *Optics Spektroskopy* **75** 712 (1993)
130. Balasubramanian K, Li J *J. Chem. Phys.* **88** 4979 (1988)
131. Bicchi P, Marinelli C, Bernheim R *J. Chem. Phys.* **97** 8809 (1992)
132. Ross A et al. *J. Phys. B* **19** L145 (1986)
133. Li L et al. *J. Chem. Phys.* **93** 8452 (1990); *Chem. Phys. Lett.* **179** 417 (1991)
134. Kowalczyk P, Katern A, Engelke F *Z. Phys. D* **17** 47 (1990); *Chem. Phys. Lett.* **146** 325 (1988)
135. Jong G et al. *J. Mol. Spectrosc.* **154** 229, 324 (1992)
136. Allegrini M et al. *Nuovo Cim. D* **10** 721 (1993)
137. La Rocgue P et al. *J. Chem. Phys.* **84** 6627 (1986)
138. Ediger M, Eden J *Chem. Phys. Lett.* **126** 158 (1986); *J. Chem. Phys.* **85** 1757 (1986)
139. Loginov A V, Solov'eva G S *Optics Spektroskopy* **63** 263 (1987); Loginov A V ibid, **76** 351 (1994)
140. Geohegan D, Eden J *J. Chem. Phys.* **89** 3410 (1988)
141. Giesel W et al. *J. Phys. B* **24** 4203 (1991)
142. Barakat B et al. *J. Mol. Spectrosc.* **116** 271 (1986)
143. Hemmerling B et al. *Z. Phys. D* **5** 165 (1987)
144. Schwarz M, Duchowicj R, Demtroder N *J. Chem. Phys.* **89** 5460 (1988)
145. Kiyashi I, Shunji K, Hajeme K *J. Chem. Phys.* **95** 8803 (1991)
146. Lipton C et al. *J. Mol. Spectrosc.* **151** 159 (1992)
147. Roche A, Jungen C *J. Chem. Phys.* **98** 3637 (1993)
148. Yiannopoulou A et al. *J. Chem. Phys.* **101** 3581 (1994)
149. Bauschlicher C et al. *J. Chem. Phys.* **92** 5377 (1990)
150. Lauferwald H, Radermann K *Ber. Bunsenges. Phys. Chem.* **96** 1273 (1992)
151. Kirkwood A et al. *J. Phys. Chem.* **95** 2644 (1991)
152. Von Niessen W *J. Chem. Phys.* **85** 337 (1986)
153. Sharpe S, Johnson P *J. Chem. Phys.* **85** 4943 (1986)
154. Roncin J Y, Launay F, Yoshino K *J. Mol. Spectrosc.* **134** 390 (1989)
155. Roux F, Michaud F *J. Mol. Spectrosc.* **136** 205 (1989)
156. Ubachs W, Tashiro L, Zare R N *Chem. Phys.* **130** 1 (1989)
157. Kam A et al. *Phys. Rev. A* **40** 1279 (1989)
158. McCormack E et al. *Phys. Rev. A* **44** 3007 (1991)
159. Lin L, Su C, Armentrout P *Chem. Phys. Lett.* **180** 168 (1991)
160. Scholl T et al. *J. Mol. Spectrosc.* **152** 398 (1992)
161. Huber K et al. *J. Chem. Phys.* **98** 4471 (1993)
162. Erman P et al. *J. Phys. B* **26** 4483 (1993)
163. Babaky O, Hussein K *Can. J. Phys.* **67** 912 (1989)
164. Rafi M, Ahmed K, Khan I, Husain M *Nuovo Cim. D* **13** 455 (1991)
165. Da X, Ueda K, Takamura H *Rev. Laser Eng.* **10** 476 (1991)
166. Borgas C, Vialle J, Broyer M *Phys. Rev. Lett.* **64** 1223 (1991)
167. Barrow R et al. *Chem. Phys. Lett.* **183** 94 (1991)
168. Fellows C et al. *Z. Phys.* **32** 321 (1995)
169. Klyagina A P et al. *J. Structural Chemistry* **28** 31 (1987)
170. James A et al. *J. Chem. Phys.* **99** 8504 (1993); **101** 4485 (1994)
171. Walter W, Schaller U, Langhoff H *J. Chem. Phys.* **83** 1667 (1985)
172. Kane D J et al. *Phys. Rev. A* **39** 4906 (1989); Kim S et al. *J. Chem. Phys.* **95** 3887 (1991); **96** 1016 (1992)
173. Bauschlicher C, Patridge H, Langhoff S *Chem. Phys. Lett.* **195** 360 (1992)
174. Chung S, Lin C, Lee ETP *Phys. Rev. A* **39** 2367 (1989)
175. Darvesh K, Fricker P, Boyd R *Chem. Phys.* **154** 99 (1991)
176. Yokelson R, Lipert R, Chupka W *J. Chem. Phys.* **97** 6144, 6153 (1992)
177. de Brouckere G, Feller D, Brion J *J. Phys. B* **27** 1657 (1994)
178. Howe J, Ashfold M, Hudgens J *J. Chem. Phys.* **101** 833 (1994)
179. Baranov S V et al *Optics Spektroskopy* **66** 277 (1989)
180. Berg L et al. *Phys. Scripta* **52** 1047 (1994)
181. Balasubramanian K *J. Chem. Phys.* **89** 6310 (1988)
182. Balasubramanian K *J. Chem. Phys.* **87** 6573 (1987)
183. Taylor S, Lemura G *J. Chem. Phys.* **89** 5517 (1988)
184. Amiot C, Crozet P, Verges J *J. Chem. Phys.* **93** 8591 (1990)
185. Spiegelmann F, Pavolini D, Daudey J *J. Phys. B* **22** 2465 (1989)
186. Cline R A, Miller J D, Heinzen D J *Phys. Rev. Lett.* **73** 632 (1994)
187. Illas F et al. *J. Chem. Phys.* **93** 2603 (1990)
188. Balasubramanian K, Das K *J. Chem. Phys.* **95** 2568 (1991)
189. Toshiaki M, Takahiro K *J. Chem. Phys.* **83** 3798 (1985)
190. Liao C, Ng C *J. Chem. Phys.* **84** 778 (1986)
191. Ramanamma C, Mahajan C *J. Mol. Spectrosc.* **145** 308 (1991)
192. Yoo R, Ruscic B, Berkowitz J *J. Chem. Phys.* **99** 8445 (1993)
193. Fursova V et al. *Chem. Phys. Lett.* **116** 317 (1985)
194. Jaworska M, Nowakowski J *Acta Phys. Pol. A* **74** 223 (1988)
195. Wang L S *Chem. Phys. Lett.* **158** 297 (1989)
196. Stolyarov A et al. *J. Mol. Spectrosc.* **137** 251 (1989)
197. Balasubramanian K *J. Chem. Phys.* **91** 5166 (1989)
198. Bhanuprakash K, Hirsh G, Buenker R *Mol. Phys.* **72** 1185 (1991)
199. Fink E et al. *Can. J. Phys.* **72** 919 (1994)
200. Bauschlicher C, Langhoff S *J. Chem. Phys.* **87** 2919 (1987)
201. Lüthi H, McLean A *Chem. Phys. Lett.* **135** 352 (1987)
202. Kitsopoulos T et al. *J. Chem. Phys.* **95** 1441 (1991)
203. Pacchoni G *Mol. Phys.* **55** 211 (1985)
204. Ho J, Polak M, Lineberger W C *J. Chem. Phys.* **96** 144 (1992)
205. Bordas C et al. *Chem. Phys. Lett.* **193** 539 (1992)
206. Pardo A et al. *Opt. Pure y Appl.* **21** 147 (1988)
207. Babaky O, Hussein K *Can. J. Phys.* **69** 57 (1991)
208. Martinez E et al. *J. Phys. B* **26** 2777 (1993)
209. Bauschlicher C et al. *J. Chem. Phys.* **95** 1057 (1991)
210. Arrington G et al. *J. Chem. Phys.* **97** 7087 (1992)
211. Nagvi A *J. Chem. Phys.* **82** 2217 (1985)
212. Fursova V D et al. *Bull. Acad. Sci. USSR, Div. of Chem. Sci.* **34** 1874 (1985)
213. Spain E, Behm J, Morse M *J. Chem. Phys.* **96** 2511 (1992)
214. Hu Z D et al. *J. Chem. Phys.* **97** 8811 (1992)
215. Dehmer P, Pratt S, Dehmer J *J. Phys. Chem.* **91** 2593 (1987)
216. Tsukiyama K, Tsukakoshi M, Kasuya T *J. Mol. Spectrosc.* **151** 312 (1992)
217. Gerasimov G N et al. *Usp. Fiz. Nauk* **162** (5) 123 (1992) [*Sov. Phys. Usp.* **35** 400 (1992)]
218. Pibel C, Yamanouchi K, Tsuchiya S *J. Chem. Phys.* **100** 6153 (1994)
219. Green D, Wallace S *J. Chem. Phys.* **100** 6129 (1994)
220. Gutsev G L *Bull. Acad. Sci. USSR, Div. of Chem. Sci.* **38** 75 (1989)
221. Kedzierski W, Atkinson J, Krause L *Chem. Phys. Lett.* **181** 427 (1991)
222. Kedzierski W, Atkinson J, Krause L *Chem. Phys. Lett.* **200** 103 (1992)
223. Balasubramanian K, Ravimohan C *J. Chem. Phys.* **92** 3659 (1990)
224. Arrington C et al. *J. Chem. Phys.* **98** 1398 (1994)
225. Drzaic P C, Marks J, Brauman J I, in *Gas Phase Ion Chemistry* (Ed. M T Bowers) (Orlando: Academic Press, 1984) p. 167
226. McHugh K M et al. *J. Chem. Phys.* **91** 3792 (1989)
227. Leopold D G, Lineberger W C *J. Chem. Phys.* **85** 51 (1986)
228. Leopold D G, Millre T M, Lineberger W C *J. Am. Chem. Soc.* **108** 178 (1986)
229. Ho J, Ervin K M, Lineberger W C *J. Chem. Phys.* **93** 6987 (1990)
230. Leopold D G, Ho J, Lineberger W C *J. Chem. Phys.* **86** 1715 (1987)
231. Snodgrass J T et al. *J. Phys. Chem.* **93** 1249 (1989)
232. Snodgrass J T et al. *Chem. Phys. Lett.* **122** 352 (1985)
233. Nimlos M R, Harding L B, Ellison G B *J. Chem. Phys.* **87** 5116 (1987)
234. Moran S, Ellison G B *J. Phys. Chem.* **92** 1794 (1988)
235. Gantefor G et al. *Z. Phys. D* **9** 253 (1988)
236. Travers M J, Cowles D C, Ellison G B *Chem. Phys. Lett.* **164** 449 (1989)
237. Ervin K M, Lineberger W C *J. Phys. Chem.* **95** 1167 (1991)
238. Kisopoulos T M et al. *J. Chem. Phys.* **95** 1441 (1991)
239. Dai D, Balasubramanian K *J. Chem. Phys.* **98** 7098 (1993)
240. Yoo R K, Ruscic B, Berkowitz J *J. Chem. Phys.* **96** 6696 (1992)
241. Wang L S et al. *J. Chem. Phys.* **93** 6310 (1990)
242. Dyke J M et al. *J. Chem. Soc. Faraday Trans.* **82** 637 (1986)
243. Amiot C *J. Chem. Phys.* **93** 8591 (1990)
244. Beutel V et al. *J. Chem. Phys.* **98** 2699 (1993)
245. Page R H, Gudeman C S *J. Chem. Phys.* **94** 39 (1991)
246. Winstead C B, Paukstis S J, Gole J L *Chem. Phys. Lett.* **237** 81 (1995)
247. Boo B H, Armantrout P B *J. Am. Chem. Soc.* **109** 3549 (1987)