SOVIET PHYSICS JETP VOLUME 27, NUMBER 5 NOVEMBER, 1968

# ROTATIONAL AND VIBRATIONAL EXCITATION OF MOLECULAR IONS BY ELECTRONS

R. F. BOĬKOVA and V. D. OB''EDKOV

Leningrad State University

Submitted November 29, 1967

Zh. Eksp. Teor. Fiz. 54, 1439–1444 (May, 1968)

The excitation of rotational and vibrational states of diatomic molecular ions is considered in the Born–Coulomb approximation. A ''direct'' nonresonance excitation mechanism of the molecules is assumed. The transition cross section is represented in the form of a sum of partial moments of the radial matrix elements. The sum can be evaluated exactly for dipole molecules and yields an analytic expression for the excitation cross section. For quadrupole molecules the result has been obtained in terms of elementary functions in the vicinity of the excitation threshold or higher. The vibrational excitation cross sections for $H_2^+$ and $HeH^+$ ions are calculated. Their maximum values are respectively $1.3 \times 10^{-16}$ and $7.1 \times 10^{-16}$ cm$^2$.

THE excitations of neutral molecules were considered theoretically in many papers. In particular, Massey[1] obtained the first results on the excitation of polar molecules, while Gerjuoy and Stein[2] calculated in the Born approximation the cross sections for the excitation of molecules with zero dipole moment, but with vanishing quadrupole moment. A complete review of the investigations is contained in the paper of Takayanagi[3]. The excitation of molecular ions has apparently not been investigated so far. An exception is the work of Stabler[4], who obtained the cross section for rotational excitation of quadrupole molecular ions in the case of extremely low energies. In the present paper we obtain formulas for the calculation of the cross sections of the vibrational and rotational excitations of dipole and quadrupole molecular ions. The limits of applicability of the obtained formulas are indicated. By way of illustration, we calculate the cross sections of the vibrational excitation of the molecules $H_2^+$ and $HeH^+$.

## 1. CHOICE OF PERTURBATION AND BASIS FUNCTIONS

We consider the excitation process

$$AB^+(vJM) + e \to AB^+(v'J'M') + e, \tag{1}$$

where v, v′, J, J′, M, and M′ are the vibrational, total rotational, and azimuthal rotational quantum numbers of the molecule. The Hamilton operator of this system is represented in the form (using atomic units)

$$\hat{H} = \hat{H}_i(\mathbf{r}_i, \mathbf{R}) - \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} - \frac{Z_b}{|\mathbf{r} - \mathbf{R}_b|} + \sum_{i=1}^{Z_a+Z_b-1} \frac{1}{|\mathbf{r} - \mathbf{r}_i|} - \frac{1}{2}\nabla_{\mathbf{r}}^2, \tag{2}$$

where $\hat{H}_i(\mathbf{r}_i, \mathbf{R})$—ion operator, $\mathbf{r}_i$, $\mathbf{r}$, $\mathbf{R}_a$, and $\mathbf{R}_b$—vectors of the molecular electrons, the incoming electron, and the nuclei of the atoms, reckoned from the center of mass of the molecule, and R—internuclear distance.

Since we plan to use a perturbation-theory formalism, we choose the energy operator of the unperturbed system in the form

$$\hat{H}_0 = \hat{H}_i(\mathbf{r}_i, \mathbf{R}) - {}^1\!/_2\nabla_{\mathbf{r}}^2 - 1/r. \tag{3}$$

Such a choice makes it possible to take into account exactly the distortion of the incident wave by the Coulomb field. The remaining part of the electrostatic interaction, in accordance with this analysis, is responsible for the excitations and can be taken into account in most cases in the first order of perturbation theory. Cases when this approximation may turn out to be insufficient will be noted separately. The operator

$$\hat{\mathscr{H}} = -\frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} - \frac{Z_b}{|\mathbf{r} - \mathbf{R}_b|} + \frac{1}{r} + \sum_{i=1}^{Z_a+Z_b-1} \frac{1}{|\mathbf{r} - \mathbf{r}_i|} \tag{4}$$

is the perturbation. We shall assume, as usual, that the wave functions of the molecular ion can be represented in the Born-Oppenheimer approximation and consequently the eigenfunction of the operator $\hat{H}_0$ will be of the form

$$\Psi(\mathbf{r}_i, \mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r}_i, \mathbf{R})\varphi_v(\mathbf{R})Y_{JM}(\hat{\mathbf{R}})F_{\mathbf{k}}(\mathbf{r}). \tag{5}$$

Here $\psi_{el}(\mathbf{r}_i, \mathbf{R})$ is the wave function of the molecular electrons, $\varphi_v(\mathbf{R})$ and $Y_{JM}(\hat{\mathbf{R}})$ are the vibrational and rotational functions of the nuclei of the molecule, and $F_{\mathbf{k}}(\mathbf{r})$ is the Coulomb function of the continuous spectrum. We note that violation of the Born-Oppenheimer approximation is significant in problems involving the capture of a continuum electron in the bound state, autoionization, etc. Inasmuch as we are considering only ''direct'' and not resonant excitations, the Born-Oppenheimer approximation for such processes can be regarded as valid, and the energy levels can be regarded as stationary.

## 2. TRANSITION CROSS SECTION

In first-order perturbation theory the differential cross section of the transition kvJ → k′v′J (k—wave vector of the incident electron) is

$$d\sigma(vJ \to v'J') = \frac{1}{4\pi^2}\frac{k'}{k}\sum_{MM'}\frac{1}{(2J+1)}|\langle\Psi^-|\hat{\mathscr{H}}|\Psi^+\rangle|^2\, d\Omega. \tag{6}$$

In this formula it is assumed that the functions $\Psi^-$ and $\Psi^+$ contain functions of the continuous spectrum, normalized to the unity density at infinity and containing divergent spherical waves in the initial state and converging ones in the final state.

The matrix $V = \langle\psi_{el}|\hat{H}|\psi_{el}\rangle$ plays the role of the potential energy of the electron-ion interaction responsible for the transition. At the distances $r > r_i$ we have

$$V = \sum_{\lambda=1}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{1}{r^{\lambda+1}} Q_{\lambda\mu}(R) P_{\lambda\mu}(\widehat{\mathbf{rR}}) e^{i\mu\varphi}, \tag{7}$$

where $Q_{\lambda\mu}$ is the $\lambda\mu$-moment of the charge distribution of the ion; when account is taken of the axial symmetry of the ions in question in the expansion (7), we have $\mu = 0$ and only the sum of the multipoles over $\lambda$ remains. The quantities $Q_1(R)$ and $Q_2(R)$ are respectively the dipole and quadrupole moments of the molecule. In the region $r < r_i$ the potential of the interaction is determined by many physical factors and is actually unknown. For this reason, V is used in the entire region of values of r (an analogous approximation in the electron-atom collision theory was introduced by Bethe). A certain justification of this procedure is connected with a small contribution of the region $r < r_i$, which follows from the analysis of the matrix elements of V and from the experience with the numerical calculations (see, for example,[5]).

Let us consider now the matrix element

$$J_{\mathbf{k}'\mathbf{k}} = \langle \mathbf{k}' | V | \mathbf{k} \rangle = \left\langle \mathbf{k}' \middle| \sum_{\lambda=1}^{\infty} Q_\lambda r^{-\lambda-1} P_\lambda(\widehat{\mathbf{rR}}) \middle| \mathbf{k} \right\rangle. \tag{8}$$

Here

$$\begin{aligned} |\mathbf{k}\rangle = F_{\mathbf{k}}^{+}(\mathbf{r}) &= e^{-\pi\eta/2}\Gamma(1+i\eta)e^{i\mathbf{kr}}F(-i\eta, 1, i(kr-\mathbf{kr})) \\ &= \sum_{lm} 4\pi(-)^m i^l e^{i\sigma_l} Y_{l-m}(\widehat{\mathbf{kz}}) Y_{lm}(\widehat{\mathbf{zr}}) (kr)^{-1} F_l(kr), \end{aligned} \tag{9}$$

$$F_l(kr) = e^{-\pi\eta/2}\frac{|\Gamma(l+1+i\eta)|}{2(2l+1)!}(2kr)^{l+1}e^{-ikr}F(l+1-i\eta, 2l+2, 2ikr) \tag{10}$$

and analogously for $|\mathbf{k}'\rangle$ 1). The z axis is reckoned from the mass center and lies in the plane of the vectors **k** and **k**′;

$$\eta = -1/k. \tag{11}$$

integrating with respect to r in (8), we get

$$J_{\mathbf{k}'\mathbf{k}} = \sum_{\lambda\mu lml'm'} Q_\lambda a^{\lambda\mu}_{lml'm'} Y^{*}_{\lambda\mu}(\widehat{\mathbf{zR}}) Y_{l-m}(\widehat{\mathbf{kz}}) Y_{l'm'}(\widehat{\mathbf{k'z}}) M^{-\lambda-1}_{ll'}, \tag{12}$$

where

$$M^{-\lambda-1}_{ll'} = \frac{1}{kk'}\int_0^\infty F_{l'}(k'r) r^{-\lambda-1} F_l(kr)\, dr, \tag{13}$$

$$\begin{aligned} a^{\lambda\mu}_{lml'm'} = \frac{(4\pi)^{5/2}}{2\lambda+1}(-)^\mu e^{i\varphi}[(2l+1)(2l'+1)(2\lambda+1)]^{1/2} \\ \times \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & \lambda \\ m & -m' & \mu \end{pmatrix}. \end{aligned} \tag{14}$$

The round brackets denote the Wigner 3j-symbols, and $\varphi$ is a phase factor which is of no importance in what follows.

We calculate

$$I = \langle \varphi_{v'} Y_{J'M'} | J_{\mathbf{k}'\mathbf{k}} | Y_{JM}\varphi_v \rangle. \tag{15}$$

Choosing the z axis in the direction of the vector k, we find that

$$I = \sum_{\lambda\mu ll'} b^{\lambda\mu}_{ll'JJ'MM'} Y_{l'\mu}(\widehat{\mathbf{kk'}}) M^{-\lambda-1}_{ll'}, \tag{16}$$

where

$$\begin{aligned} b^{\lambda\mu}_{ll'JJ'MM'} = \frac{(2l+1)^{1/2}}{4\pi}\langle v' | Q_\lambda | v \rangle a^{\lambda\mu}_{l0l'\mu}[(2J+1)(2J'+1)(2\lambda+1)]^{1/2}\cdot \\ \times \begin{pmatrix} J & J' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & J' & \lambda \\ M & M' & -\mu \end{pmatrix}. \end{aligned} \tag{17}$$

We then set up the product $II^*$, integrating the result with respect to $d\Omega$ and summing over M and M′, so that we get

$$\sum_{MM'} \int |I|^2 d\Omega = \sum_{\lambda ll'} c^{\lambda}_{ll'JJ'} |M^{-\lambda-1}_{ll'}|^2. \tag{18}$$

Here

$$\begin{aligned} c^{\lambda}_{ll'JJ'} = \frac{(4\pi)^3}{(2\lambda+1)} |\langle v' | Q_\lambda | v \rangle|^2 (2l+1)(2l'+1)(2J+1)(2J'+1) \\ \times \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} J & J' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2. \end{aligned} \tag{19}$$

This result is connected in obvious fashion with the total cross section. We finally get for $\sigma$

$$\begin{aligned} \sigma &= \sum_{\lambda=1}^{\infty} \sigma_\lambda, \\ \sigma_\lambda(vJ \to v'J') &= 16\pi\frac{k'}{k}|\langle v' | Q_\lambda | v \rangle|^2 \frac{2J'+1}{2\lambda+1} \begin{pmatrix} J & J' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\times \sum_{ll'} (2l+1)(2l'+1) \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 |M^{-\lambda-1}_{ll'}|^2. \end{aligned} \tag{20}$$

## 3. DIPOLE TRANSITIONS

Let us consider electric dipole excitation of the molecule ($\lambda = 1$). In this special case, the matrix element (8) coincides with the corresponding matrix element in the theory of dipole bremsstrahlung, and can be calculated exactly, this being equivalent to summation over $ll'$ in (20). We obtain

$$\begin{aligned} &\sum_{ll'} (2l+1)(2l'+1) \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 |M^{-\lambda-1}_{ll'}|^2 \\ &= \frac{\pi^2}{2kk'} \frac{\exp(2\pi\eta)}{[\exp(2\pi\eta)-1][\exp(2\pi\eta')-1]} x_0 \frac{d}{dx_0} |F(-i\eta, -i\eta', 1, x_0)|^2 \\ &\equiv \frac{E}{4\Delta E}\frac{1}{kk'}\sigma_0\left(\Delta E, \frac{E}{\Delta E}\right). \end{aligned} \tag{21}$$

In formula (21) $x_0 = -4\eta\eta'/(\eta' - \eta)^2$, $E = k^2/2$, $\sigma_0$ is a function tabulated in[7], for values $2^{-5} \leq \Delta E \leq \infty$ and $1.01 \leq E/\Delta E \leq 5.0$.

The cross section of the dipole transition takes the form

$$\sigma_1 = \frac{2\pi}{3\Delta E}|\langle v' | Q_1 | v \rangle|^2 (2J'+1) \begin{pmatrix} J & J' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma_0. \tag{22}$$

For the rotational excitation $vJ \to vJ \pm 1$ it follows therefore that

$$\sigma_1^{rot}(J \to J \pm 1) = \frac{2\pi Q_1^2}{3\Delta E} g_\pm \sigma_0, \tag{23}$$

where

$$g_\pm = \begin{cases} (J+1)/(2J+1) & \text{for excitation } J \to J+1 \\ J/(2J+1) & \text{for de-excitation } J \to J-1. \end{cases}$$

For vibrational transitions we have in the harmonic approximation for the vibrations of the nuclei

---

1) All references connected with the use of Coulomb functions can be found in the paper by Alder et al.[6]

$$\langle v'|Q_1(R)|v\rangle = \left(\frac{\partial Q_1}{\partial R}\right)_{R_0}\langle v'|R|v\rangle = \left(\frac{\partial Q_1}{\partial R}\right)_{R_0}\left(\frac{v+1}{2m\omega}\right)^{1/2}, \quad (24)$$

where m—reduced mass of the nuclei and ω—oscillation frequency, $v' = v + 1$.

The cross section of the vibrational excitation, summed over the final rotational states, is

$$\sigma_1^{vibr}(v \rightarrow v+1) = \frac{\pi}{3m\omega}\left(\frac{\partial Q_1}{\partial R}\right)_0^2 \frac{v+1}{\Delta E}\sigma_0. \quad (25)$$

## 4. QUADRUPOLE TRANSITIONS

For quadrupole transitions $\lambda = 2$. Then in the sum over $ll'$ in (20) there remain the values $l' = l \leq 1$ or $l' = l \pm 2$. The integral for $M_{ll}^{-3}$ (see[6] is expressed in terms of the generalized hypergeometric functions $F_2(\alpha, \beta, \gamma, \delta, \epsilon; x, y)$ and $F_3(\alpha, \beta, \gamma, \delta, \epsilon; 1/x, 1/y)$ of two variables, and can be obtained numerically. Under certain relations between the parameters, however, or in certain energy intervals, the result can be obtained in terms of elementary functions.

We consider the region of greatest physical interest—in the vicinity of the threshold of excitation and above. We introduce the quantity

$$\xi = \frac{\Delta E}{2E}\frac{1}{k'}. \quad (26)$$

In the vicinity of the threshold of $\Delta E/E \lesssim 1$ and $k'' \ll 1$, so that the condition $\pi\xi \gg 1$ is always well satisfied. Under this condition we get

$$|M_{ll}^{-3}|^2 = \frac{\pi^2}{[l(l+1)(2l+1)]^2}\frac{1}{kk'}[1 + O(e^{-\pi\xi})]. \quad (27)$$

The values of the integrals $M_{ll\pm 2}^{-3}$ can be obtained with the aid of the recurrence relations for the integrals $M_{ll}$. It turns out here that $M_{ll\pm 2} \propto k^2 M_{ll}$, and therefore their contribution to the cross section is negligibly small in the energy region under consideration ($k^2 < 1$).

From (20) we get for the cross section of the rotational transition

$$\sigma_2^{rot}(J \rightarrow J \pm 2) = \frac{\pi Q_2^2}{k^2} g_\pm(J),$$

$$g_\pm(J) = (2J + 4 \pm 1)\begin{pmatrix} J & J\pm 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \cdot 0{,}567. \quad (28)$$

In this formula, the largest limiting values of $k^2$ for a specified transition $\Delta E$ are determined from the condition $\pi\xi > 1$. Introducing the rotational constant $B_V$, we rewrite this condition in the form

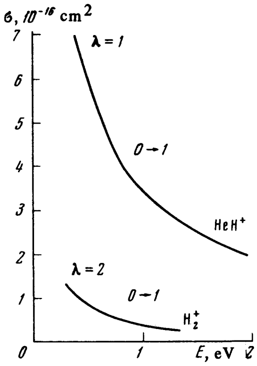
$$4\pi B_v(J+1)/k^3 > 1. \quad (29)$$

Inasmuch as $B_V$ is of the order of $10^{-4}$, we should have for the wave number $k \lesssim 0.1$. Under these conditions the cross section $\sigma_2^{rot} \gtrsim 100\, Q^2 g\pi$. For elastic scattering ($J \rightarrow J$) the cross section $\sigma_2^{el}$ diverges as $k \rightarrow 0$.

We proceed to vibrational excitation of quadrupole molecules. For the transition cross section summed over all the rotational states, we get

$$\sigma_2^{vibr} = \frac{0{,}284\pi}{m\omega k^2}(v+1)\left(\frac{\partial Q_2}{\partial R}\right)_{R_0}^2, \quad (30)$$

under the condition $\pi\xi > 1$. For vibrational transitions, this condition limits the maximum value of $k^2$ to energies on the order of several electron volts.



## 5. CERTAIN EXAMPLES

Let us apply the results to the molecules $H_2^+$ and $HeH^+$. The necessary spectroscopic and quantum-mechanical data for $H_2^+$ are widely known, and those for $HeH^+$ were taken from the paper by Anex[8]. The obtained results are shown in the figure for the 0 → 1 transition. There are neither experimental data on ion excitation nor other theoretical calculations. From the considered examples it follows that the cross section for the excitation of dipole transitions is larger by approximately one order of magnitude than the cross section of quadrupole excitations, this being in agreement with the general notions. In order to verify the feasibility of obtaining data for the quadrupole transition, let us compare this cross section with the theoretical limit. Practically the entire contribution to this cross section is due to the partial wave $l = 1$, and consequently the calculated cross sections should not exceed, in any case, the value $3\pi/k^2$. Therefore, according to (30), the ratio

$$\Delta = \frac{0.284}{3m\omega}\left(\frac{\partial Q_2}{\partial R}\right)_{R_0}^2 (v+1)$$

should be smaller than unity. The conditions for the applicability of perturbation theory in the general case requires satisfaction of the condition $\Delta \ll 1$. In our example $\Delta \sim 0.01$, from which we can conclude that the result is valid within the framework of the initial approximations.

In conclusion, the authors are deeply grateful to Yu. N. Demkov, G. F. Drukarev, and V. S. Egorov for a discussion of the work.

---

[1] H. S. W. Massey, Proc. Cambr. Phil. Soc. 28, 99 (1932).

[2] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).

[3] K. Takayanagi, J. Phys. Soc. Japan 21, 3 (1966).

[4] R. C. Stabler, Phys. Rev. 131, 679 (1963).

[5] A. Dalgarno and R. J. W. Henry, Proc. Phys. Soc. 85, 679 (1965).

[6] K. Adler, A. Bohr, T. Huus, B. Mottelson, and A. Winther, Rev. Mod. Phys. 28, 432 (1956).

[7] M. K. Gaĭlitis, in: Atomnye stolknoveniya (Atomic Collisions), AN LatvSSR, Riga, 1963, p. 93.

[8] B. G. Anex, J. Chem. Phys. 38, 1661 (1963).

Translated by J. G. Adashko