

ENERGY OF INTERACTION BETWEEN A DIATOMIC MOLECULE AND LIGHT

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By transforming to new variables and carrying out a multipole expansion of the interaction Hamiltonian, we obtain expressions for the multipole moments of the molecule. The transition matrix elements are given.

1. Molecular spectroscopy treats the molecule in terms of translational, rotational, vibrational, and electronic degrees of freedom. To proceed to this kind of description the molecular Hamiltonian must be reexpressed in terms of the so-called molecular coordinates¹. In considering the interaction between the molecule and the electromagnetic field, it would seem natural to represent the interaction energy in the same variables, which would provide an insight into the field effect on the different degrees of freedom, the dependence of the interaction on the molecular structure and composition, and the contributions of the electron and nuclear subsystem to the interaction. Quite a bit of attention has been given to the description of the molecular coordinates (see, e.g. Refs. 2–8). Unlike any articles the authors are aware of so far, the present paper deals with a diatomic molecule interacting with an optical field. In so doing, special interest emphasis is laid on the tensor structure of the interaction in view of current topical problems pertaining, for instance, to the optical orientation of the molecules.

By transforming to new variables and using a multipole expansion of the interaction Hamiltonian we derive expressions for the multipole moments of the molecules and calculate the matrix elements of the transitions involved.

2. Let us consider a neutral diatomic molecule with nuclear charges z_1e and z_2e (e is the absolute charge of the electron) and masses m_1 and m_2 interacting with a quantized electromagnetic field described by the vector $\vec{A}(\vec{r})$ and scalar $\varphi(\vec{r})$ potentials in the Lorentzian gauge. The interaction Hamiltonian expressed in the laboratory coordinate system within the framework of the linear (in the electromagnetic field) approximation reads

$$H = -\sum_{\alpha} \frac{e_{\alpha}}{m_{\alpha}c} \mathbf{A}(\mathbf{r}_{\alpha}) \mathbf{p}_{\alpha} + \sum_{\alpha} e_{\alpha} \varphi(\mathbf{r}_{\alpha}) - \sum_j \mu_j \mathbf{H}(\mathbf{r}_j), \quad (1)$$

where $\mu_j = -\frac{e}{mc} s_j$ (s_j is the spin of the j -th electron); $H(r)$ is the magnetic field strength).

We make the following substitutions of variables in Eq. (1):

$$\mathbf{r}_{1,2} = \mathbf{R} \pm \frac{\mu}{m_{1,2}} \mathbf{r} - \frac{m}{M} \sum_j \mathbf{r}_j; \quad \mathbf{r}_1 = \mathbf{R} + \mathbf{r}_1 - \frac{m}{M} \sum_j \mathbf{r}_j, \quad (2)$$

where \mathbf{R} is the radius vector of the molecular center of inertia with respect to the laboratory reference frame; $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, \mathbf{r}_j are the radius vectors of electrons referred to from the nuclear center of mass; μ is the equivalent mass and M is the total molecular mass. Note that the angular variables are not introduced in explicit form here. The multipole expansion of Eq. (1) then gives in the dipole approximation

$$H^{(0)} = -\frac{e}{c} \mathbf{A}(\mathbf{R}) \left[\left(\frac{z_1}{m_1} - \frac{z_2}{m_2} \right) \mathbf{p}_r - \frac{M}{M_N m} \sum_j \pi_j \right] + e \left[\left(\frac{z_1}{m_1} - \frac{z_2}{m_2} \right) \mu \mathbf{r} - \sum_j \mathbf{r}_j \right] \nabla_{\mathbf{R}} \varphi(\mathbf{R}), \quad (3)$$

where \bar{p}_r and $\bar{\pi}_j$ it are the momenta canonically conjugate to coordinates \mathbf{r} and \mathbf{r}_j , respectively; $M_N = m_1 + m_2$. Instead of a conventional interaction operator Eq. (3) contains interaction terms with both constant and variable dipole moments. The form of the resulting expression explicitly shows the dependence of the interaction on the isotopic composition of the molecule. For homonuclear molecules in a fixed electronic state the dipole transitions, as is well known, are forbidden. In this case, as can be seen from Eq. (3), in transitions between different electronic terms the field does not directly perturb the nuclear subsystem. A change in the nuclear motion results only from a change in the intramolecular Coulomb energy due to the electronic transitions. A similar situation also occurs for molecules of the CO- or NO-type where the term responsible for the interaction between the nuclei and the field is small, its difference from zero being related to the nuclear mass defect. Hence, for this kind of molecule both the interelectronic dipole transitions and those in the electronic ground state are induced by the influence of the field on the electronic subsystem.

The interaction energy subject to the next-order multipole expansion is given by the relation

$$H^{(1)} = \sum_{\kappa} (F^{\kappa} \cdot \{\nabla_{\mathbf{R}} \otimes \mathbf{A}(\mathbf{R})\}^{\kappa}) + \sum_{\kappa} (G^{\kappa} (\nabla_{\mathbf{R}} \otimes \nabla_{\mathbf{R}})^{\kappa}) \varphi(\mathbf{R}), \quad (4)$$

where (... ..) denotes the inner product of two irreducible tensors of rank κ ; $\{\dots\}^{\kappa}$ are the irreducible tensors of rank κ (Ref. 9). Tensors F and G , respectively, are given by

$$F^{\kappa} = -\frac{1}{\hbar c} \{d \otimes P\}^{\kappa} - \frac{1}{e} \frac{m}{\hbar c} \{d \otimes d\}^{\kappa} - \frac{e}{c} \left[\frac{Z_1 m_2^2 + Z_2 m_1^2}{M m_1 m_2} - \frac{m}{M} \mu \left(\frac{Z_1}{m_1} - \frac{Z_2}{m_2} \right)^2 \right] (r \otimes p_r)^{\kappa} + \frac{e}{m c} \sum_j (r_j \otimes \pi_j)^{\kappa} + \frac{e}{m c} S \delta_{\kappa,1}. \quad (5)$$

$$G^{\kappa} = \frac{e}{2} \frac{Z_1 m_2^2 + Z_2 m_1^2}{M m_1 m_2} \mu (r \otimes r)^{\kappa} - \frac{e}{2} \sum_j (r_j \otimes r_j)^{\kappa} - \frac{m}{\hbar} \left\{ d \otimes \sum_j r_j \right\}^{\kappa}, \quad (6)$$

where P is the molecular inertia center momentum, d is the dipole moment operator:

$$d = e \left[\frac{Z_1}{m_1} - \frac{Z_2}{m_2} \right] \mu r - e \sum_j r_j \quad (7)$$

with

$$\dot{d} = \frac{i}{\hbar} [H^{(0)}, d].$$

The zero-rank tensors in Eqs. (5) and (6) correspond to the intermolecular interaction through scalar and longitudinal fields. The first-rank tensor (magnetic moment) describes the magnetic dipole transitions. The first term in the magnetic moment is the transition frequency shift due to the Doppler effect and is of the order of v/c . The second term determines the transition between different electronic terms satisfying the selection rule $\Delta \Lambda = \pm 1$ and is of the order of m/M . In contrast with the electron orbital moments, its selection rule is constant. The third term renormalizes the electron and nuclear g -factors and be retained when considering the rotational transitions of the Σ -terms along with the nonadiabatic contribution from the electron orbital momentum¹⁰. The second-rank tensors in Eqs. (5) and (6) determine the quadrupole transitions.

According to the Wigner-Eckart theorem, the angular dependence in the matrix elements of the operators contained in the interaction Hamiltonian is separates to yield, here

$$T^{\kappa} (T^{\kappa} = F^{\kappa}; G^{\kappa}).$$

$$\begin{aligned} \langle \alpha_1 J_1 M_1 | T^{\kappa q} | \alpha_2 J_2 M_2 \rangle &= \\ &= \langle (-1)^{J_1 - M_1} \begin{Bmatrix} J_1 & \kappa & J_2 \\ -M_1 & q & M_2 \end{Bmatrix} \langle \alpha_1 J_1 || T^{\kappa} || \alpha_2 J_2 \rangle. \end{aligned} \quad (8)$$

The irreducible matrix elements are given below using the notation adopted in the theory of diatomic molecules.

1) Type-a coupling (Hund's case (a), Ref. 11).

$$\begin{aligned} \langle n_1 \Lambda_1 S_1 v_1 J_1 \Omega_1 || T^{\kappa} || n_2 \Lambda_2 S_2 v_2 J_2 \Omega_2 \rangle &= \\ &= (-1)^{J_1 - \Omega_1} [J_1 J_2]^{1/2} \begin{Bmatrix} J_1 & \kappa & J_2 \\ -\Omega_1 & q & \Omega_2 \end{Bmatrix} \times \\ &\times \langle n_1 \Lambda_1 S_1 v_1 \Sigma_1 | T^{\kappa q} | n_2 \Lambda_2 S_2 v_2 \Sigma_2 \rangle. \end{aligned} \quad (9)$$

2) Type-b coupling (Hund's case (b), Ref. (11)).

for the spin-independent operator

$$\begin{aligned} \langle n_1 \Lambda_1 S_1 v_1 K_1 J_1 || T^{\kappa} || n_2 \Lambda_2 S_2 v_2 K_2 J_2 \rangle &= \\ &= \delta_{S_1 S_2} (-1)^{J_2 + S_1 + \kappa - \Lambda_2} [J_1 J_2 K_1 K_2]^{1/2} \begin{Bmatrix} K_1 & J_1 & S_1 \\ J_2 & K_2 & \kappa \end{Bmatrix} \begin{Bmatrix} K_1 & \kappa & K_2 \\ -\Lambda_1 & q & \Lambda_2 \end{Bmatrix} \times \\ &\times \langle n_1 \Lambda_1 v_1 | T^{\kappa q} | n_2 \Lambda_2 v_2 \rangle; \end{aligned} \quad (10)$$

and for the spin operator

$$\begin{aligned} \langle n_1 \Lambda_1 S_1 v_1 K_1 J_1 || S^1 || n_2 \Lambda_2 S_2 v_2 K_2 J_2 \rangle &= \\ &= \delta_{n_1 n_2} \delta_{\Lambda_1 \Lambda_2} \delta_{K_1 K_2} \delta_{S_1 S_2} \times \\ &\times (-1)^{J_2 + S_1 + \kappa_1} [J_1 J_2 S_1 S_2 (S_1 + 1)]^{1/2} \begin{Bmatrix} S_1 & J_1 & K_1 \\ J_2 & S_1 & 1 \end{Bmatrix}, \end{aligned} \quad (11)$$

where $\hat{J} = 2J + 1$.

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