Molecular transition moments at large internuclear distances

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The behavior of the dipole moments of molecular transitions is analyzed as a function of the internuclear distance R and it is shown that for allowed transitions the departure of the dipole moment from the value for the unperturbed atom varies as R^{-3} with a coefficient that can be obtained from the dynamic polarizability of one atom evaluated at the unperturbed transition frequency of the other.

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I. INTRODUCTION

In radiative transitions between different electronic states of diatomic molecules, the behavior of the transition moment at large internuclear distances has been little explored, with the exception of homonuclear molecules where the similarity of the atoms into which the molecule separates plays a decisive role [1]. The long range behavior of the interaction potentials and the transition moments of heteronuclear molecules is important in determining the profiles of absorption and emission lines of gaseous mixtures near the line centers [2–9]. Considerable attention has been given to the variation of the potentials with the internuclear distance R in the region of the van der Waals attraction but not to the form of the transition moments.

Explicit calculations of the transition dipole matrix elements have been carried out for several molecular systems and a wide range of internuclear distances R [8,10–14]. The resulting matrix elements tend correctly to the atom limits at large R but only rarely are they of sufficient accuracy that the variation with R can be reliably extracted.

We show here that for a heteronuclear system which separates to a pair of atoms, one of which may be excited but not the other, the departure from the limiting atom value varies as R^{-3} with a coefficient that may be obtained from the dynamic polarizability of the unexcited atom evaluated at the transition frequency of the other atom. The formula is useful in predicting the behavior of the dipole moments with R and may be useful in assessing the accuracy of *ab initio* calculations. Numerical values are presented for molecular systems resulting from the interaction of alkali metal atoms and the inert gases.

II. THEORY

We investigate the transition from an initial molecular state with electronic eigenfunction $\chi_i(\mathbf{r})$ to a final state $\chi_f(\mathbf{r})$ where $\mathbf{r}$ represents collectively the position vectors of the electrons. The transition is driven by a one-electron operator $d(\mathbf{r}_a)+d(\mathbf{r}_b)$ where $d(\mathbf{r}_a)$ and $d(\mathbf{r}_b)$ represent, respectively, the sums of the position vectors $\mathbf{r}_a$ and $\mathbf{r}_b$ of the electrons of atoms a and b into which the diatomic molecule separates at large internuclear distances R. At large R, $\chi_i(\mathbf{r};R)$ tends asymptotically to the product $\phi_i(\mathbf{r}_a)\theta_i(\mathbf{r}_b)$ and $\chi_f(\mathbf{r})$ to the product $\phi_f(\mathbf{r}_a)\theta_f(\mathbf{r}_b)$, where ϕ_i and ϕ_f are eigenfunctions of atom a and θ_i and θ_f are eigenfunctions of atom b, and the position vectors $\mathbf{r}_a$ and $\mathbf{r}_b$ may be referred to their parent nuclei: The interaction $V(\mathbf{r}_a,\mathbf{r}_b;R)$ between the atoms may be expanded as a power series in R^{-1} [15]. For dipole transitions, only the dipole-dipole term of the expansion contributes in first order. It may be written in Cartesian coordinates in the form [15]

$$V=\frac{1}{R^3}(x^a x^b+y^a y^b-2z^a z^b), \tag{1}$$

where (x^a,y^a,z^a) and (x^b,y^b,z^b) are the sums of the Cartesian coordinates of the electrons of atoms a and b, respectively, with the z axis lying along the internuclear axis. If H_a and H_b are the Hamiltonians of atoms a and b, with eigenfunctions ϕ_m and θ_n and eigenvalues E_m^a and E_n^b,

$$(H_a-E_m^a)\phi_m=0, \tag{2}$$

and

$$(H_b-E_n^b)\theta_n=0. \tag{3}$$

The first order molecular wave functions are

$$\chi_i^{(1)}=\sum_m\sum_n\frac{\langle\phi_i\theta_i|V|\phi_m\theta_n\rangle\langle\phi_m\theta_n|}{(E_i^a-E_m^a)+(E_i^b-E_n^b)}, \tag{4}$$

$$\chi_f^{(1)}=\sum_{m'}\sum_{n'}\frac{\langle\phi_f\theta_f|V|\phi_{m'}\theta_{n'}\rangle\langle\phi_{m'}\theta_{n'}|}{(E_f^a-E_{m'}^a)+(E_f^b-E_{n'}^b)}, \tag{5}$$

and the sums exclude the terms $m=n=i$ and $m'=n'=f$. To first order, the transition dipole moment is given by

$$D=D_0+D_1, \tag{6}$$

where

$$D_0=\langle\phi_i|d(\mathbf{r}_a)|\phi_f\rangle \tag{7}$$

and

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$$D_1=\sum_m \sum_n \frac{\langle \phi_i\theta_i|V|\phi_m\theta_n\rangle\langle \phi_m\theta_n|d(\mathbf{r}_a)+d(\mathbf{r}_b)|\phi_f\theta_f\rangle}{(E_i^a-E_m^a)+(E_i^b-E_n^b)}$$
$$+\sum_{m'} \sum_{n'} \frac{\langle \phi_f\theta_f|V|\phi_{m'}\theta_{n'}\rangle\langle \phi_{m'}\theta_{n'}|d(\mathbf{r}_a)+d(\mathbf{r}_b)|\phi_i\theta_i\rangle}{(E_f^a-E_{m'}^a)+(E_f^b-E_{n'}^b)}. \tag{8}$$

Because of orthogonality, the contributions are zero except when $\theta_i=\theta_f$ and D_1 reduces to the form

$$D_1=2\sum_n (E_i^b-E_n^b)\frac{\langle \phi_f\theta_i|V|\phi_i\theta_n\rangle\langle \theta_n|d(\mathbf{r}_b)|\theta_i\rangle}{(E_i^a-E_f^a)^2-(E_i^b-E_n^b)^2}. \tag{9}$$

For a transition between molecular states of Σ symmetry, the dipole-dipole term of V yields

$$D_1=\frac{4D_0}{R^3}\sum_n \frac{(E_n^b-E_i^b)|\langle \theta_i|z^b|\theta_n\rangle|^2}{(E_i^b-E_n^b)^2-\omega^2}, \tag{10}$$

where ω is the unperturbed transition energy $E_i^a-E_f^a$ of atom a. The dynamic dipole polarizability of atom b at a frequency ω may be written

$$\alpha^b(\omega)=2\sum_n \frac{(E_n^b-E_0^b)|\langle \theta_i|z^b|\theta_n\rangle|^2}{(E_n^b-E_0^b)^2-\omega^2}, \tag{11}$$

so that

$$D_1=\frac{2D_0}{R^3}\alpha^b(\omega) \tag{12}$$

and

$$D=D_0\left\{1+\frac{2}{R^3}\alpha^b(\omega)\right\}. \tag{13}$$

For Σ-Π transitions,

$$D=D_0\left\{1-\frac{1}{R^3}\alpha^b(\omega)\right\}. \tag{14}$$

III. RESULTS AND DISCUSSION

The dynamic polarizabilities $\alpha(\omega)$ may be derived from measurements of the refractive indices [16–19] as functions of frequency. We list in Table I the values of $\alpha(\omega)$ for the inert gases at the resonance transition frequencies of the alkali metal atoms. They differ little from the static polarizabilities evaluated at $\omega=0$.

TABLE I. Dynamic polarizabilities of the inert gases at the resonance frequencies of the alkali metals in units of a_0^3.

	He	Ne	Ar	Kr	Xe
Li	1.39	2.68	11.2	17.0	27.9
Na	1.39	2.69	11.2	17.1	28.1
K	1.39	2.68	11.2	16.9	27.7
Rb	1.39	2.68	11.2	17.0	27.7
Cs	1.39	2.68	11.2	16.9	27.6

The formulas (13) and (14) show that as R decreases inward from large distances the transition dipole moments of Σ-Σ transitions increase in magnitude and the transition dipole moments of Σ-Π transitions decrease. There have been several *ab initio* calculations of the transition dipole moments between electronic states of molecules composed of alkali metal atoms and inert gases [8,11–14]. Some are qualitatively consistent with the behavior predicted by Eqs. (13) and (14) and some are not. None is in quantitative agreement. The discrepancies may be due in part to the failure of Eqs. (13) and (14) to account for the effects of the overlaps of the electron distribution but they may also reflect inaccuracies in the description of the molecular eigenfunctions at large separations. In order to obtain the correct long range behavior of the dipole moments it is necessary that the eigenfunctions contain as a compoment the product of excited states of the inert gas accessed by a dipole transition and excited or ground states of the alkali metal atom into which the participating molecular states separate. In emission spectroscopy, important contributions arise from the region in which the van der Waals attraction dominates the interaction. It is in this region that our formula should become applicable.

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