

8-1-1987

Simple model for the resonant vibrational excitation of molecules and its application to Li₂ and N₂

J M. Wadehra

Wayne State University, ad5541@wayne.edu

P J. Drallos

Wayne State University

Recommended Citation

Wadehra JM, Drallos PJ. Simple model for the resonant vibrational excitation of molecules and its application to Li₂ and N₂. *Phys. Rev. A.* 1987;36(3):1148-1155. doi: 10.1103/PhysRevA.36.1148
Available at: http://digitalcommons.wayne.edu/phy_astro_frp/101

This Article is brought to you for free and open access by the Physics and Astronomy at DigitalCommons@WayneState. It has been accepted for inclusion in Physics and Astronomy Faculty Research Publications by an authorized administrator of DigitalCommons@WayneState.

Simple model for the resonant vibrational excitation of molecules and its application to Li₂ and N₂

J. M. Wadehra and P. J. Drallos

Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48202

(Received 2 February 1987)

A simple model for the resonant vibrational excitation of a molecule by electron impact is proposed in which the potential curves of the electronic states of the molecule and its resonant anion are replaced by those of linear harmonic oscillators of arbitrary frequencies and equilibrium internuclear separations. A closed-form expression for the excitation amplitude is derived. Useful recursion relations among amplitudes are obtained which allow convenient evaluation of cross sections for any inelastic or superelastic vibrational transition. The model is used to generate the cross sections for vibrational excitation of Li₂ and N₂ by the impact of low-energy electrons.

I. INTRODUCTION

It has been well established that the phenomenon of vibrational excitation of a molecule by electron impact is dominated by resonance formation.¹ The direct (or non-resonant) contribution, which is quite important for the elastic scattering of electrons by a molecule, to the vibrational excitation is usually small. For example, the spectacular peaks in the cross sections for vibrational excitation of molecular nitrogen can be satisfactorily reproduced only by using a proper resonance model.² The purpose of this paper is to present a closed-form expression for the resonant contribution to the amplitude for vibrational excitation of a molecule by electron impact using a simple model. Furthermore, some useful recursion relations among the excitation amplitudes will be obtained which will permit a rapid evaluation of the resonant contribution to the cross sections for any inelastic or superelastic vibrational transition in a molecule.

In the model that we are proposing here, the potential curves of the electronic state of the molecule and of the resonant anion state are replaced by those of two simple harmonic oscillators of arbitrary frequencies, curvatures, and equilibrium internuclear separations. Moreover, the two oscillators have arbitrary energy separation. A similar (but not identical) model has been used in the past by other investigators^{3,4} for vibrational excitation of a molecule by an electron. In these previous investigations the two linear harmonic oscillators were taken to have the same frequency. Also, a simple recursion relation among excitation amplitudes was obtained previously⁴ and was valid only for the inelastic transitions. The results in the present paper represent a generalization of the previous results and indeed reduce to those previous results for the case of equal frequency oscillators.

Finally, the results of the present paper are used to obtain the cross sections for vibrational excitation of Li₂ and N₂ by electron impact. The model can successfully gen-

erate the experimentally observed⁵ peaks in the cross sections for nitrogen and predicts the excitation cross sections for lithium dimers.

II. VIBRATIONAL EXCITATION AMPLITUDE

In the process of vibrational excitation, a molecule *AB*, initially in the vibrational level *m*, undergoes a transition under the impact of an electron of energy $\epsilon = \hbar^2 k_i^2 / 2m_e$, to the final vibrational level *n*, leaving behind an electron with energy $\epsilon_f = \hbar^2 k_f^2 / 2m_e$. This process,

$$e(k_i) + AB(m) \rightarrow AB^- \rightarrow e(k_f) + AB(n),$$

proceeds via the formation of an intermediate resonant state *AB*⁻, whose nuclear wave function $\xi(\mathbf{R})$, in the local-width approximation, satisfies¹ (in atomic units),

$$[T_N + V^- + \Delta(\mathbf{R}) - i\Gamma(\mathbf{R})/2 - E]\xi(\mathbf{R}) = -[\Gamma/(2\pi)]^{1/2}\chi_m(\mathbf{R}). \quad (1)$$

Here, $V^-(\mathbf{R})$ is the real part of the potential curve of the anion state *AB*⁻. $\Delta(\mathbf{R})$ and $\Gamma(\mathbf{R})$ are, respectively, the level shift and the resonance width. T_N is the nuclear kinetic energy, and $\chi_m(\mathbf{R})$ is the nuclear wave function of the initial rotationless vibrational level of *AB*. E is the total energy of the system, that is, $E = \epsilon + E_m$, E_m being the initial vibrational energy of the target molecule. If $\chi_n(\mathbf{R})$ is the wave function of the final vibrational level of the molecule, the amplitude for vibrational excitation via resonance formation is¹

$$A(m \rightarrow n; \epsilon) = B \langle n | [\Gamma(\mathbf{R})/(2\pi)]^{1/2} | \xi(\mathbf{R}) \rangle, \quad (2)$$

where $B = -4\pi^2/(k_i k_f)^{1/2}$. For brevity, we are using the bra and ket notation to denote the various vibrational wave functions of the molecule, namely, $\chi_m(\mathbf{R}) = \langle \mathbf{R} | m \rangle$ and $\chi_n(\mathbf{R}) = \langle \mathbf{R} | n \rangle$. Using Eq. (1) and introducing a complete set of vibrational wave functions $\langle\langle \mathbf{R} | v \rangle\rangle$ of the anion state, the transition amplitude can be written as

$$A(m \rightarrow n; \epsilon) = -B \sum_v \langle n | [\Gamma(\mathbf{R})/2\pi]^{1/2} [E_v + \Delta(\mathbf{R}) - i\Gamma(\mathbf{R})/2 - E]^{-1} | v \rangle \langle\langle v | [\Gamma(\mathbf{R})/2\pi]^{1/2} | m \rangle\rangle, \quad (3)$$

where the sum over ν includes integration over the continuum nuclear functions of the resonant anion electronic state. E_ν is the energy of the ν th vibrational level of the anion. In what follows, we will consistently use the doublet ket notation (such as $| \nu \rangle\rangle$) to denote the vibrational wave functions of the resonant state and a single ket notation (such as $| m \rangle$ or $| n \rangle$) to denote the vibrational wave functions of the neutral target state. Now, if the width Γ and the level shift Δ , which in general are energy dependent, are taken to be independent of the internuclear separation \mathbf{R} and energy ϵ , then Eq. (3) can be written as

$$A(m \rightarrow n; \epsilon) = -2\pi \left[\frac{\Gamma^2}{k_i k_f} \right]^{1/2} \sum_\nu \frac{\langle n | \nu \rangle \langle \nu | m \rangle}{E - E_\nu + i\Gamma/2 - \Delta}. \quad (4)$$

Note that $\langle n | \nu \rangle$ and $\langle \nu | m \rangle$ are essentially the Franck-Condon overlap integrals between the vibrational levels of the initial electronic state of the target and those of the resonant anion state.

Now we introduce a simple model in which the potential curves of the initial electronic state of the target and the resonant anion state are taken to be those of simple linear harmonic oscillators of frequencies ω and ω_- , respectively. r is the separation between the equilibrium internuclear positions of the two oscillators. Figure 1 shows the two potential curves and their relative geometry. The overlap integrals, along with useful recursion relations, between vibrational levels of two off-center linear harmonic oscillators of different frequencies have been worked out in detail.⁶ For the case of linear oscillators, Eq. (4) for the vibrational transition amplitude becomes

$$A(m \rightarrow n; \epsilon) = -\frac{2\pi}{\omega_-} \left[\frac{\Gamma^2}{k_i k_f} \right]^{1/2} a(m \rightarrow n; \epsilon), \quad (5a)$$

where

$$a(m \rightarrow n; \epsilon) = \sum_{\nu=0}^{\infty} \frac{\langle n | \nu \rangle \langle \nu | m \rangle}{Q - \nu} \quad (5b)$$

and $Q = [\epsilon - \delta E + m\omega + (\omega - \omega_-)/2 - \Delta + i\Gamma/2]/\omega_-$. δE is defined in Fig. 1. Either one of the two overlap in-

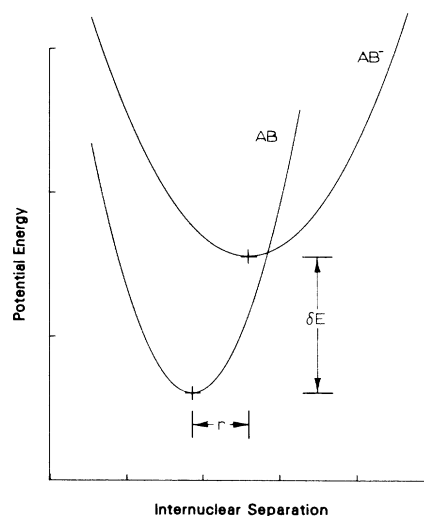


FIG. 1. Schematic representation of the potential energy curves of the molecule AB and its resonant anion AB^- by linear harmonic oscillators.

tegrals appearing in Eq. (5b) can be written in a closed form as a finite sum.⁶ Evaluation of $a(m \rightarrow n; \epsilon)$ will then involve two finite sums and an infinite sum. As we will show now, $a(m \rightarrow n; \epsilon)$ can be alternatively obtained, using the recursion relations which will be derived below, from the mere knowledge of $a(0 \rightarrow 0; \epsilon)$ and $a(0 \rightarrow 1; \epsilon)$. Furthermore, $a(0 \rightarrow 0; \epsilon)$ and $a(0 \rightarrow 1; \epsilon)$ can each be written as simple one-dimensional integrals which can be evaluated rapidly on a computer for any electron impact energy ϵ . To begin with, we define a few convenient relations:

$$\gamma = \frac{\omega - \omega_-}{\omega + \omega_-}, \quad \omega_0 = \hbar/(\mu r^2), \quad \alpha^2 = \omega\omega_- / [\omega_0(\omega_-^2 - \omega^2)],$$

$$\beta^2 = \omega^2\omega_- / [\omega_0(\omega^2 - \omega_-^2)], \quad (6)$$

where μ is the reduced mass of the nuclei in the molecule AB . Now the Franck-Condon overlap integral $\langle m | \nu \rangle$, using the two-center harmonic oscillator wave functions, is⁶

$$\langle m | \nu \rangle = N (2^{m+\nu} m! \nu!)^{-1/2} \sum_{k=0}^{[m,\nu]} \binom{m}{k} \binom{\nu}{k} \gamma^{(\nu-k)/2} (-\gamma)^{(m-k)/2} (1-\gamma^2)^{k/2} k! H_{m-k}(\alpha) H_{\nu-k}(-\beta) 2^k, \quad (7)$$

where

$$N = \left[\frac{2(\omega\omega_-)^{1/2}}{\omega + \omega_-} \right]^{1/2} \exp \left[\frac{-\omega\omega_-}{2\omega_0(\omega + \omega_-)} \right],$$

H_m are the Hermite polynomials and $[m, \nu]$ denotes the smaller of the two integers m and ν . Substituting Eq. (7) into Eq. (5) and interchanging the order of the sums, one obtains

$$a(m \rightarrow n; \epsilon) = N^2 (2^{m+n} m! n!)^{-1/2} \sum_{k=0}^m \binom{m}{k} \gamma^{-k/2} (-\gamma)^{(m-k)/2} (1-\gamma^2)^{k/2} k! 2^k H_{m-k}(\alpha)$$

$$\times \sum_{l=0}^n \binom{n}{l} \gamma^{-l/2} (-\gamma)^{(n-l)/2} (1-\gamma^2)^{l/2} l! 2^l H_{n-l}(\alpha)$$

$$\times \sum_{\nu=\{k,l\}}^{\infty} \binom{\nu}{k} \binom{\nu}{l} \gamma^{\nu} [2^{\nu} \nu! (Q - \nu)]^{-1} H_{\nu-k}(-\beta) H_{\nu-l}(-\beta), \quad (8)$$

where $\{k, l\}$ denotes the larger of the two integers k and l . Using Eq. (A4), $a(m \rightarrow n; \varepsilon)$ can be written as

$$a(m \rightarrow n; \varepsilon) = N^2 (2^m + n m! n!)^{-1/2} \sum_{k=0}^m \binom{m}{k} \gamma^{-k/2} (-\gamma)^{(m-k)/2} (1-\gamma^2)^{k/2} H_{m-k}(\alpha) \\ \times \sum_{l=0}^n \binom{n}{l} \gamma^{-l/2} (-\gamma)^{(n-l)/2} (1-\gamma^2)^{l/2} H_{n-l}(\alpha) \left[\frac{\partial}{\partial x} \right]_{x=-\beta}^k \left[\frac{\partial}{\partial y} \right]_{y=-\beta}^l A_{00}(x, y), \quad (9)$$

where

$$A_{00}(x, y) = \sum_{\nu=0}^{\infty} \frac{\gamma^{\nu} H_{\nu}(x) H_{\nu}(y)}{2^{\nu} \nu! (Q - \nu)}. \quad (10)$$

On using the integral representation,

$$\int_0^{\infty} \exp[i(Q - \nu)t] dt = \frac{i}{Q - \nu}, \quad \text{Im} Q > 0 \quad (11)$$

and the bilinear generating function for the Hermite polynomials, Eq. (A3), $A_{00}(x, y)$ can be rewritten as

$$A_{00}(x, y) = -i \int_0^{\infty} \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{\gamma^2(x^2 - 2xyz/\gamma + y^2)}{\gamma^2 - z^2} \right]. \quad (12)$$

Here, for convenience, we have introduced $z = \exp(it)$. Now the derivatives in Eq. (9) can be carried out explicitly and using Eqs. (12) and (A2), we find

$$\left[\frac{\partial}{\partial x} \right]_{x=-\beta}^k \left[\frac{\partial}{\partial y} \right]_{y=-\beta}^l A_{00}(x, y) = -i \int_0^{\infty} \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2 \gamma}{z + \gamma} \right] \\ \times \sum_{p=0}^{[k, l]} \binom{k}{p} \binom{l}{p} \left[\frac{2\gamma z}{z^2 - \gamma^2} \right]^p p! \left[\frac{\gamma}{(z^2 - \gamma^2)^{1/2}} \right]^{k+l-2p} \\ \times H_{k-p} \left\{ - \left[\beta^2 \left[\frac{z - \gamma}{z + \gamma} \right] \right]^{1/2} \right\} H_{l-p} \left\{ - \left[\beta^2 \left[\frac{z - \gamma}{z + \gamma} \right] \right]^{1/2} \right\}. \quad (13)$$

Substituting from Eq. (13) into Eq. (9) and interchanging the sums again, one obtains

$$a(m \rightarrow n; \varepsilon) = -i N^2 (2^m + n m! n!)^{-1/2} \int_0^{\infty} \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2 \gamma}{z + \gamma} \right] \sum_{p=0}^{[m, n]} \left[\frac{2\gamma z}{z^2 - \gamma^2} \right]^p p! \\ \times \sum_{k=p}^m \binom{m}{k} \binom{k}{p} (-\gamma)^{(m-k)/2} \left[\frac{1-\gamma^2}{\gamma} \right]^{k/2} H_{m-k}(\alpha) \left[\frac{\gamma}{(z^2 - \gamma^2)^{1/2}} \right]^{k-p} H_{k-p} \left\{ - \left[\beta^2 \left[\frac{z - \gamma}{z + \gamma} \right] \right]^{1/2} \right\} \\ \times \sum_{l=p}^n \binom{n}{l} \binom{l}{p} (-\gamma)^{(n-l)/2} \left[\frac{1-\gamma^2}{\gamma} \right]^{l/2} H_{n-l}(\alpha) \left[\frac{\gamma}{(z^2 - \gamma^2)^{1/2}} \right]^{l-p} H_{l-p} \left\{ - \left[\beta^2 \left[\frac{z - \gamma}{z + \gamma} \right] \right]^{1/2} \right\}. \quad (14)$$

Finally, using Eq. (A5) twice to carry out the k and l sums and then applying Eq. (A6), the final result is obtained:

$$A(m \rightarrow n; \varepsilon) = \frac{-iBN^2}{2\omega - \pi} \left[\frac{\Gamma^2}{2^m + n m! n!} \right]^{1/2} \sum_{p=0}^{[m, n]} \binom{m}{p} \binom{n}{p} p! 2^p \\ \times \int_0^{\infty} \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2 \gamma}{z + \gamma} \right] \left[\frac{1 - \gamma z}{z - \gamma} \right]^p \left[\frac{\gamma(1 - z^2)}{z^2 - \gamma^2} \right]^{(m+n-2p)/2} \\ \times H_{m+n-2p} \left[\left[\alpha^2 \frac{(z-1)(z-\gamma)}{(z+1)(z+\gamma)} \right]^{1/2} \right]. \quad (15)$$

Equation (15) reduces to a single term for the case in which either m or n is zero. For example, the two important special cases, $A(0 \rightarrow 0; \varepsilon)$ and $A(0 \rightarrow 1; \varepsilon)$, are

$$A(0 \rightarrow 0; \varepsilon) = \frac{-iBN^2 \Gamma}{2\omega - \pi} \int_0^{\infty} \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2 \gamma}{z + \gamma} \right], \quad (16)$$

$$A(0 \rightarrow 1; \varepsilon) = \frac{-iBN^2\Gamma}{2\omega_- \pi} \int_0^\infty \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2\gamma}{z + \gamma} \right] \left[\frac{z-1}{z+\gamma} \right] \left[\frac{(1-\gamma^2)\omega_-}{2\omega_0} \right]^{1/2}. \quad (17)$$

For the case in which both m and n are equal to one, we obtain

$$A(1 \rightarrow 1; \varepsilon) = \frac{-iBN^2\Gamma}{4\omega_- \pi} \int_0^\infty \frac{dt z^{Q+1}}{(z^2 - \gamma^2)^{1/2}} \exp \left[\frac{2\beta^2\gamma}{z + \gamma} \right] \left[\frac{z(1-\gamma^2)}{z+\gamma} \right] \left[\frac{2}{z-\gamma} + \frac{\omega_-(z-1)^2}{z\omega_0(z+\gamma)} \right]. \quad (18)$$

From these amplitudes [Eqs. (16) through (18)], and from the recursion relations to be derived below, the entire matrix for vibrational excitation amplitudes can be obtained (see Sec. III).

For the case in which the oscillator frequencies of both the neutral state and the resonant state are the same (that is, $\omega = \omega_-$), the integral in Eq. (15) can be carried out. The resulting expression for the vibrational amplitude in this case becomes

$$A(m \rightarrow n; \varepsilon) = \frac{-BN^2\Gamma}{\pi 2\omega(m!n!)^{1/2}} \sum_{p=0}^{[m,n]} \begin{bmatrix} m \\ p \end{bmatrix} \begin{bmatrix} n \\ p \end{bmatrix} p! \left[\frac{\omega}{2\omega_0} \right]^{(m+n-2p)/2} \frac{\Gamma(p-Q)\Gamma(m+n-2p+1)}{\Gamma(m+n-p-Q+1)} \\ \times \Phi(p-Q, m+n-Q-p+1; \omega/(2\omega_0)). \quad (19)$$

Here, Φ is the confluent hypergeometric function. This expression was obtained earlier for the case $m=0$ and n arbitrary by Golubkov *et al.*,³ and in the alternative form of continued fractions for the case $m=n=0$ by Domcke and Cederbaum.⁷

III. RECURSION RELATIONS

For the special case in which the frequencies of the two oscillators are equal ($\omega = \omega_-$), a three-term recursion relation among the vibrational amplitudes was derived by Domcke and Cederbaum.⁷ More general recursion relations among the amplitudes, for the case in which the oscillator frequencies are not the same ($\omega \neq \omega_-$), are obtained below. The recursion relation of Domcke and Cederbaum is a special case of these general recursion relations.

The vibrational amplitude can be written as a sum of Franck-Condon overlap integrals as in Eq. (4) if the width and the level shift are taken to be independent of \mathbf{R} . Recursion relations among these Franck-Condon integrals have been obtained previously^{6,8} and can be written as

$$(n+1)^{1/2}(\omega + \omega_-) \langle n+1 | v+1 \rangle - 2[\omega\omega_-(v+1)]^{1/2} \langle n | v \rangle \\ + n^{1/2}(\omega_- - \omega) \langle n-1 | v+1 \rangle - \omega_-(2\omega/\omega_0)^{1/2} \langle n | v+1 \rangle = 0, \quad (20)$$

$$[2(v+1)]^{1/2} \langle n | v+1 \rangle = \left[\frac{n}{2\omega\omega_-} \right]^{1/2} (\omega + \omega_-) \langle n-1 | v \rangle - \left[\frac{n+1}{2\omega\omega_-} \right]^{1/2} (\omega - \omega_-) \langle n+1 | v \rangle \\ - \left[\frac{\omega_-}{\omega_0} \right]^{1/2} \langle n | v \rangle. \quad (21)$$

Using Eq. (21), the terms containing $|v+1\rangle$ in Eq. (20) can be eliminated, resulting in a five-term recursion relation in which the index v stays constant. Thus,

$$[2n(\omega^2 + \omega_-^2) - 4\omega\omega_-(v+1) + (\omega + \omega_-)^2 + 2\omega\omega_-^2/\omega_0] \langle n | v \rangle \\ - 2\omega_-^2(2\omega/\omega_0)^{1/2} [(n+1)^{1/2} \langle n+1 | v \rangle + n^{1/2} \langle n-1 | v \rangle] \\ - (\omega^2 - \omega_-^2) \{ [(n+1)(n+2)]^{1/2} \langle n+2 | v \rangle + [n(n-1)]^{1/2} \langle n-2 | v \rangle \} = 0. \quad (22)$$

Equation (22) can be used to obtain recursion relations for the vibrational excitation amplitudes. Multiply Eq. (22) by $\langle m | v \rangle / (Q-v)$ and sum over v to get

$$\sum_{v=0}^{\infty} \langle m | v \rangle \langle n | v \rangle \left[2n(\omega^2 + \omega_-^2) + 4\omega\omega_-(Q-v) - 4\omega\omega_-(Q+1) + (\omega + \omega_-)^2 + \frac{2\omega\omega_-^2}{\omega_0} \right] / (Q-v) \\ - 2\omega_-^2 \left[\frac{2\omega}{\omega_0} \right]^{1/2} \left[(n+1)^{1/2} \sum_{v=0}^{\infty} \frac{\langle m | v \rangle \langle v | n+1 \rangle}{Q-v} + n^{1/2} \sum_{v=0}^{\infty} \frac{\langle m | v \rangle \langle v | n-1 \rangle}{Q-v} \right] \\ - (\omega^2 - \omega_-^2) \left[[(n+1)(n+2)]^{1/2} \sum_{v=0}^{\infty} \frac{\langle m | v \rangle \langle v | n+2 \rangle}{Q-v} + [n(n-1)]^{1/2} \sum_{v=0}^{\infty} \frac{\langle m | v \rangle \langle v | n-2 \rangle}{Q-v} \right] = 0, \quad (23)$$

where $4\omega\omega_-Q$ has been added and subtracted in the numerator of the first term. This first term can be rewritten as

$$\begin{aligned} & \sum_{v=0}^{\infty} \langle m | v \rangle \langle v | n \rangle \left[2n(\omega^2 + \omega_-^2) + 4\omega\omega_-(Q-v) - 4\omega\omega_-(Q+1) + (\omega + \omega_-)^2 + \frac{2\omega\omega_-^2}{\omega_0} \right] / (Q-v) \\ &= \left[2n(\omega^2 + \omega_-^2) - 4\omega\omega_-(Q+1) + (\omega + \omega_-)^2 + \frac{2\omega\omega_-^2}{\omega_0} \right] \sum_{v=0}^{\infty} \frac{\langle m | v \rangle \langle v | n \rangle}{Q-v} + 4\omega\omega_- \sum_{v=0}^{\infty} \langle m | v \rangle \langle v | n \rangle. \end{aligned} \quad (24)$$

Using the completeness relation on the second term in Eq. (24) and using Eq. (5) we obtain the following recursion relation:

$$\begin{aligned} & \left[2n(\omega^2 + \omega_-^2) - 4\omega\omega_-(Q+1) + (\omega + \omega_-)^2 + \frac{2\omega\omega_-^2}{\omega_0} \right] a(m \rightarrow n; \epsilon) + 4\omega\omega_- \delta_{m,n} \\ & - 2\omega_-^2 (2\omega/\omega_0)^{1/2} [(n+1)^{1/2} a(m \rightarrow n+1; \epsilon) + n^{1/2} a(m \rightarrow n-1; \epsilon)] \\ & - (\omega^2 - \omega_-^2) \{ [(n+1)(n+2)]^{1/2} a(m \rightarrow n+2; \epsilon) + [n(n-1)]^{1/2} a(m \rightarrow n-2; \epsilon) \} = 0. \end{aligned} \quad (25)$$

Note that in this five-term recursion relation among vibrational excitation amplitudes, the initial vibrational level m and the incident electron energy ϵ is fixed in each term. This, of course, implies that the total energy $E = \epsilon + E_m$ is the same in each term as it should be. It is possible to obtain an alternative recursion relation among the amplitudes in which the final vibrational level n is fixed in each term. Such a relationship can be obtained by replacing n by m in Eq. (22), multiplying the resulting equation by $\langle n | v \rangle / (Q-v)$, and summing over v . Additional care must be taken in this case because the factor Q in the denominator contains m . The resulting recursion relation is

$$\begin{aligned} & \left[2m(\omega^2 + \omega_-^2) - 4\omega\omega_-(Q+1) + (\omega + \omega_-)^2 + \frac{2\omega\omega_-^2}{\omega_0} \right] a(m \rightarrow n; \epsilon) + 4\omega\omega_- \delta_{m,n} \\ & - 2\omega_-^2 (2\omega/\omega_0)^{1/2} [(m+1)^{1/2} a(m+1 \rightarrow n; \epsilon - \omega) + m^{1/2} a(m-1 \rightarrow n; \epsilon + \omega)] \\ & - (\omega^2 - \omega_-^2) \{ [(m+1)(m+2)]^{1/2} a(m+2 \rightarrow n; \epsilon - 2\omega) + [m(m-1)]^{1/2} a(m-2 \rightarrow n; \epsilon + 2\omega) \} = 0. \end{aligned} \quad (26)$$

Note that the initial vibrational level m is different in various terms but the final level n is fixed. Furthermore, the incident electron energy is different, although the total energy E is the same in each term of the recursion relation.

The principle of detailed balancing relates the amplitude of the m -to- n transition to the amplitude of the n -to- m transition, albeit at different incident electron energy (but at the same total energy), as

$$A(m \rightarrow n; \epsilon) = A(n \rightarrow m; \epsilon + (m-n)\omega). \quad (27)$$

It is easy to see that Eq. (27) also follows from Eq. (5) almost by inspection.

From the mere knowledge of the two vibrational amplitudes, $A(0 \rightarrow 0; \epsilon)$ and $A(0 \rightarrow 1; \epsilon)$ at all energies, and using the recursion relation of Eq. (25), the entire first row ($m=0$) of the vibrational amplitude matrix can be obtained. Equation (27) can then be applied to obtain the first column ($n=0$). With the additional knowledge of $A(1 \rightarrow 1; \epsilon)$, the next row (or column) can be obtained using Eq. (25) [or Eq. (26)]. Here, it should be noted that there are two alternative methods for completing the amplitude matrix. First, the rows and columns of the entire matrix can be obtained by successive use of the recursion relations of Eqs. (25) and (26). Second, using the principle of detailed balancing, Eq. (27), each column (or row) can be obtained from its corresponding row (or column). Thus only half of the matrix needs to be built up via the recursion relations.

IV. DISCUSSION

In the preceding sections we have obtained a summation expression, Eq. (5), and an integral expression, Eq. (15), for the amplitude for resonant vibrational excitation of a molecule. Useful five-term recursion relations among these amplitudes are obtained in Eqs. (25) and (26) which, from a mere knowledge of amplitudes for transitions to only three low-lying levels, would permit a rapid evaluation of vibrational excitation cross sections for any transition, inelastic or superelastic, for any molecule.

The summation expression of Eq. (5) proved to be more useful than the integral expressions of Eqs. (16) and (17) when used for evaluation of the amplitudes. This is because the integrands in Eqs. (16) and (17) for $A(0 \rightarrow 0; \epsilon)$ and $A(0 \rightarrow 1; \epsilon)$ are rapidly oscillating and require a prohibitive number of evaluations in order to obtain sufficient accuracy to be used with the recursion relations. The summation expression, Eq. (5), on the other hand, achieves similar accuracy after typically including only 25 terms in the sum, and is to be preferred *numerically*. Although the integral expression may not appear useful numerically, it can be seen from Eq. (9) that if $A_{00}(x, y)$ could be evaluated analytically, then all of the higher-order transition amplitudes can be determined exactly by merely taking derivatives of A_{00} . The recursion relations, Eqs. (25) and (26), can be used for generating the amplitudes for excitation of higher vibrational levels if $a(0 \rightarrow 0; \epsilon)$, $a(0 \rightarrow 1; \epsilon)$, and $a(1 \rightarrow 1; \epsilon)$ are known either

from the summation expression, Eq. (5), or from the integral expression, Eq. (15). These recursion relations become especially useful for the integral expressions because the real and imaginary parts of the integrals representing the lowest-order transition amplitudes ($0 \rightarrow 0$, $0 \rightarrow 1$, and $1 \rightarrow 1$) are easily separable. Furthermore, use of complex algebra and evaluation of Hermite polynomials can be avoided in obtaining the higher-order transition amplitudes. It should be noted that use of the recursion relations [Eq. (26), in particular] requires that the step size in electron-impact energy should be some proper fraction of the oscillator excitation energy $\hbar\omega$.

For the case when the frequencies of the two oscillators representing the potential curves of the molecule and its anion are equal, the recursion relation, Eq. (25), reduces to a three-term relation and is identical to the one obtained by Domcke *et al.*⁴ This three-term recursion relation among amplitudes is essentially equivalent to a recursion relation among confluent hypergeometric functions⁹ since for the case of equal-frequency oscillators the excitation amplitude is related to a confluent hypergeometric function as seen in Eq. (19). As far as we know, the second recursion relation, Eq. (26), that we have obtained, in which the *final* vibrational level is fixed, has not been obtained earlier in the literature for either equal or unequal frequency oscillators. In obtaining Eq. (4) for the excitation amplitude it was assumed that the width of the resonance is independent of the internuclear separation. This assumption led to the Franck-Condon overlap integrals in Eq. (4) and to the recursion relations in Eqs. (25) and (26) which are merely extensions of the recursion relations among the Franck-Condon integrals. If, however, the width Γ depends on the internuclear separation, more general recursion relations among excitation amplitudes can still be obtained by using the recursion relations among two-center harmonic-oscillator matrix elements.⁶

In order to illustrate the utility of the recursion relations derived above, we have numerically evaluated the vibrational excitation amplitudes for Li_2 and N_2 using Eqs. (5), (7), and (25). The vibrational excitation cross sections obtained from these amplitudes are displayed in Figs. 2 and 3, respectively. The parameters for the potential curves of the ground and the resonant anion states for the two molecules¹⁰⁻¹² used in these calculations are listed in Table I. Note that the width of the resonance Γ is taken to be energy independent. The level shift Δ is taken to be zero. It is easy to verify that the first five vibrational levels of the above simple harmonic oscillators have the same energy levels, within 5%, as the actual vibrational energy levels of the ground electronic states of the molecules. This indicates that the harmonic-oscillator approximation is reasonable for these levels. The parameters ω , ω_- , r , and δE of the lithium system are taken from the recent *ab initio* calculations¹² of the structure of the ground and excited states of Li_2 and Li_2^- using the optimized configuration-interaction (CI) wave functions. Following Wigner's threshold law, the width $\Gamma(R)$ of the resonant state is taken to be of the form $\Gamma(R) = ck(R)$, where $k(R)$ is the wave number of the electron autodetaching at internuclear separation R . The constant c is determined¹² by, first, smoothly extrapolating the fully optimized orbital

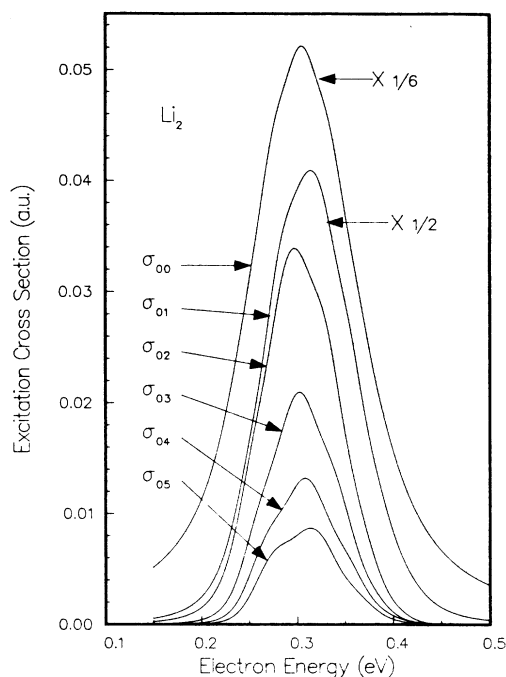


FIG. 2. Cross sections for the resonant vibrational excitation of Li_2 by the impact of low-energy electrons.

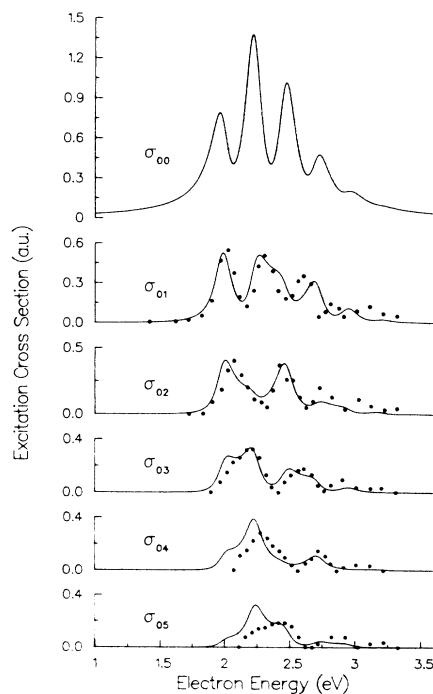


FIG. 3. Cross sections for the resonant vibrational excitation of N_2 by the impact of low-energy electrons. Solid circles represent the experimental values of the respective cross sections from Ref. 5.

TABLE I. Potential curve parameters in atomic units. The numbers in square brackets represent powers of ten.

Parameter	Li ₂	N ₂
ω	1.5983[−3]	1.073[−2]
ω_-	1.0519[−3]	8.82[−3]
r	8.0623[−1]	1.638[−1]
μ	6.426[+3]	1.2852[+4]
δE	9.4979[−3]	7.38699[−2]
Γ	2.273[−3]	6.5[−3]

exponents of the CI wave functions from the variationally stable region into the autodetaching region. This procedure yields estimates of the matrix elements coupling the discrete resonant state and the continuum states which, in turn, are related to the resonance width via Fermi's golden rule. In the present calculations, $\Gamma(R_0)$, where R_0 is the equilibrium internuclear separation of Li₂, is taken as the constant width of the resonant state of Li₂[−]. The values of the parameters ω , ω_- , and δE for the molecular nitrogen system are taken from the *ab initio* calculations as listed in Ref. 11. The parameters r and Γ were adjusted by starting from the initial values of Golubkov *et al.*,³ such that the calculated vibrational excitation cross sections agreed as best with the experimental values as possible.

Figure 2 shows the cross sections for vibrational excitation of Li₂ by the impact of low-energy electrons. Molecular lithium is isovalent with molecular hydrogen and is known to exhibit characteristics similar to those of molecular hydrogen in regard to the process of dissociative attachment, which is another resonant process.¹³ The lowest resonant state of Li₂[−] is the $A^2\Sigma_g^+$ state. In the case of molecular hydrogen it is known¹⁴ that the contribution of the $^2\Sigma_g^+$ resonant state to the vibrational excitation cross sections shows a structureless peak for any inelastic transition. It is thus not surprising, based on the similarities between Li₂ and H₂, that the inelastic excitation cross sections for Li₂ as shown in Fig. 2 are also almost structureless. All of the cross sections show only one peak, and the location of the peak is roughly the same for all transitions. Also, there is the possible development of a second peak in the higher-order transitions [$A(0 \rightarrow 4; \epsilon)$ and $A(0 \rightarrow 5; \epsilon)$]. Figure 3 shows the cross sections for the vibrational excitation of molecular nitrogen by the impact of low-energy electrons dominated by the $^2\Pi_g$ resonance of N₂[−]. Because of the boomerang nature of this resonance, the vibrational excitation cross sections exhibit a series of spectacular peaks.⁵ It is to be noticed that the present model can successfully account for occurrence and locations of these peaks in the cross sections for low-lying transitions. The present model is not expected to reproduce the cross sections for excitations to higher vibrational levels¹⁵ due to the effects of anharmonicity.

The assumption of constant Γ in the present calculations is made for convenience only. Even if Γ depends on the internuclear separation R in some simple analytical manner, it might be possible⁶ to carry out the two-center harmonic-oscillator matrix elements analytically. At first

sight, the assumption of constant Γ may appear quite drastic since in the case of N₂ it has been well established,¹¹ using the boomerang model, that features of the excitation cross sections are best obtained when the resonance width is taken as a decreasing function of the internuclear separation. Then, a strong interference between the single incident and a single reflected nuclear wave packet leads to peaks in the vibrational excitation cross sections of N₂ which shift to larger energies for excitation to higher levels. However, since the present model is expected to be accurate only for low-lying vibrational levels, the convenient (but not necessary) assumption of constant Γ is reasonable. Furthermore, since all of the results are analytic, it is hoped that the present model with recursion relations could be useful for calculations of excitation cross sections in polyatomic molecules for which *ab initio* calculations are relatively tedious.

Finally, we comment on the applicability of the present model for obtaining resonant contributions to the vibrational excitation of a molecule. The starting point of the present model is the local equation, Eq. (1), which implies that the model is valid for energies not too close to the threshold. Use of a harmonic oscillator to represent the potential curves implies that the present model would work best for obtaining cross sections for vibrational transitions among low-lying levels only. For transitions to higher vibrational levels where the effects of anharmonicity become important, a similar useful model using Morse oscillators could possibly be developed.

ACKNOWLEDGMENT

The support of the U.S. Air Force Office of Scientific Research through Grant No. AFOSR-84-0143 is gratefully acknowledged.

APPENDIX

Some of the useful properties of Hermite polynomials that have been used in various derivations are collected here.⁹ From the linear generating function of Hermite polynomials,

$$\sum_{n=0}^{\infty} H_n(x)t^n/n! = \exp(-t^2 + 2xt), \quad (\text{A1})$$

the following representation for Hermite polynomials is obtained:

$$H_n(B/A) = A^{-n}(\partial/\partial t)_t^n \exp(-A^2t^2 + 2Bt). \quad (\text{A2})$$

The bilinear generating function of Hermite polynomials is

$$(1-z^2)^{-1/2} \exp\left[y^2 - \frac{(y-zx)^2}{1-z^2}\right] = \sum_{n=0}^{\infty} \frac{H_n(x)H_n(y)z^n}{2^n n!}. \quad (\text{A3})$$

The derivatives of the Hermite polynomials are given by

$$\frac{d}{dx} H_n(x) = 2nH_{n-1}(x). \quad (\text{A4})$$

A couple of useful sums of these polynomials are

$$\sum_{m=j}^s \begin{pmatrix} s \\ m \end{pmatrix} \begin{pmatrix} m \\ j \end{pmatrix} \alpha_1^{m-j} H_{m-j}(x_1) \alpha_2^{s-m} H_{s-m}(x_2) = (\alpha_1^2 + \alpha_2^2)^{(s-j)/2} H_{s-j} \left(\frac{\alpha_1 x_1 + \alpha_2 x_2}{(\alpha_1^2 + \alpha_2^2)^{1/2}} \right) \begin{pmatrix} s \\ j \end{pmatrix} \quad (\text{A5})$$

and

$$\sum_{p=0}^{[m,n]} \begin{pmatrix} m \\ p \end{pmatrix} \begin{pmatrix} n \\ p \end{pmatrix} p! g^p H_{m-p}(x) H_{n-p}(x) = \sum_{p=0}^{[m,n]} \begin{pmatrix} m \\ p \end{pmatrix} \begin{pmatrix} n \\ p \end{pmatrix} p! (2+g)^p H_{m+n-2p}(x) . \quad (\text{A6})$$

-
- ¹J. M. Wadehra, in *Nonequilibrium Vibrational Kinetics*, edited by M. Capitelli (Springer-Verlag, Heidelberg, 1986), p. 191.
- ²B. I. Schneider, *Phys. Rev. A* **14**, 1923 (1976).
- ³G. V. Golubkov, F. I. Dalidchik, and G. K. Ivanov, *Zh. Eksp. Teor. Fiz.* **73**, 439 (1977) [*Sov. Phys.—JETP* **46**, 230 (1977)].
- ⁴W. Domcke, L. S. Cederbaum, and F. Kasper, *J. Phys. B* **12**, L359 (1979).
- ⁵G. J. Schulz, *Phys. Rev.* **135**, A988 (1964).
- ⁶P. J. Drallos and J. M. Wadehra, *J. Chem. Phys.* **85**, 6524 (1986).
- ⁷W. Domcke and L. S. Cederbaum, *J. Phys. B* **13**, 2829 (1980); **14**, 149 (1981).
- ⁸F. Ansbacher, *Z. Naturforsch., Teil A* **14**, 889 (1959).
- ⁹W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer-Verlag, New York, 1966).
- ¹⁰K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
- ¹¹L. Dube and A. Herzenberg, *Phys. Rev. A* **20**, 194 (1979); A. U. Hazi, T. N. Rescigno, and M. Kurilla, *ibid.* **23**, 1089 (1981).
- ¹²H. H. Michels, R. H. Hobbs, and L. A. Wright, *Chem. Phys. Lett.* **118**, 67 (1985); H. H. Michels (private communication).
- ¹³J. M. Wadehra, in *Proceedings of the Fourth International Symposium on the Production and Neutralization of Negative Ions and Beams*, edited by J. Alessi (AIP, New York, 1987).
- ¹⁴J. N. Bardsley and J. M. Wadehra, *Phys. Rev. A* **20**, 1398 (1979).
- ¹⁵M. Allan, *J. Phys. B* **18**, 4511 (1985).