Resonant Vibrational Excitation of N_2 by Low-Energy Electrons: An *Ab Initio R*-Matrix Calculation

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The resonant vibrational excitation of N_2 by low-energy electrons is used to illustrate the newly developed R-matrix theory of vibrational excitation and dissociative attachment of Schneider, Le Dourneuf, and Burke. The *ab initio* calculations are performed which clearly illustrate the role of the internal states in describing these excitation processes and support the authors' contention that the essential physics is completely contained within a Born-Oppenheimer treatment of the total molecular Hamiltonian.

Quite recently a new theory of vibrational excitation and dissociative attachment has been proposed by Schneider, Le Dourneuf, and Burke.[1] This theory, based on the R-matrix method, provides a more complete description of the mechanism of these processes than has been possible in the past. If we assume that the Born-Oppenheimer separation of electronic and nuclear motion holds for the compound system in the strong-interaction, small-distance range, the previously developed fixed-nuclei R-matrix theory[2] of electron-molecule scattering may be trivially extended to account for the nuclear motion. In this Letter we intend to illustrate the reliability of the theory on the widely studied resonant vibrational excitation of N_2 by low-energy electrons. The calculations are totally *ab initio* and no attempt has been made to adjust the theoretical results to experimental information. We recall that the scattering of the electrons by N_2 in the 2-4-eV energy range is dominated by a $^2\Pi_g$ resonance in which an incident d-wave electron is trapped inside the molecule by the large centrifugal barrier. This shape resonance substantially enhances the vibrational excitation cross section, the resonant structure of which has been the subject of numerous experimental[3-5] and theoretical[6-8] papers. Although the basic mechanism of the process is well understood, there is only one calculation in the literature which attempts to treat the problem from a first-principles viewpoint.[6] The difference between the R-matrix method and the vibrational close-coupling theory lies in the recognition that the internal electronic states, which are calculated in the fixed-nuclei approximation, contain all the essential information to describe the vibrational cross sections. In point of fact, earlier more phenomenological[7] models are founded on this very assumption. The R-matrix method provides a practical computational tool to calculate the internal electronic states which are at the core of these phenomenological models.

The first ingredient of the R-matrix theory remains the electronic energies and wave functions of the compound system. They are obtained as a function of internuclear distance by solving the electronic Schrödinger equation

$$[H_e + L_b - E_k(R)]\,|\psi_k\rangle = 0 \qquad (1)$$

inside a sphere containing the charge distribution of the target. By applying the variational principle to the full $(N+1)$-electron system it is possible to describe the distortion (polarization) and accompanying formation of the resonance quite simply. Figure 1 shows in full lines the

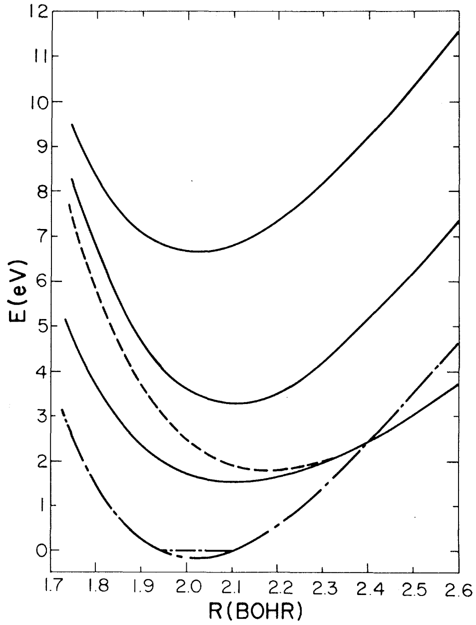

FIG. 1. Potential curves for N_2 and N_2^-: dash-dotted line, ground state of N_2; dotted line, resonant state of N_2^-; and solid line, R-matrix states of N_2^-.

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adiabatic potential curves for the first three electronic states of the $e + N_2$ complex. These curves were obtained in the single-configuration approximation with the scattered-electron wave function determined by

$$[h + L_0 - E_k(R)] | F_k) = 0, \tag{2a}$$

$$h = -\tfrac{1}{2}\nabla^2 - \frac{Z_{1A}}{r_{1A}} - \frac{Z_{1B}}{r_{1B}} + 2J - K, \tag{2b}$$

$$L_0 | F_k) = \left[\frac{\partial}{\partial r} | F_R)\right]_{r=a} = 0. \tag{2c}$$

The Coulomb and exchange operators, J and K, were calculated with core molecular orbitals taken from a self-consistent–field (SCF) optimization on the N_2^- ($^2\Pi_g$) state with vanishing derivative imposed at $a = 8a_0$. This procedure, completely justified within the R-matrix sphere allows a simple but accurate description of the strong distortions of the core orbitals in the scattering process. Outside, for the chosen sphere radius, the long-range potentials were neglected and the scattering phase shifts are simply obtained by matching to spherical Bessel and Neumann functions. The variation of the resonance position and width as a function of R are shown in Fig. 1 (dashed line) and Fig. 2, respectively. Although the strong angular-momentum mixing inside the R-matrix box is extensively accounted for in the calculation by a multicenter expansion of the F_k, only the $l = 2$ partial wave is important asymptotically. Furthermore, it is clear from Fig. 1 that the resonant N_2^- ($^2\Pi_g$) potential curve corresponds mainly to the mixing of the first two adiabatic R-matrix states. The resonant curve is flatter than the neutral N_2 potential and has its minimum shifted to larger internuclear distance. These results confirm the simple interpretation of the resonance as due to the capture of the incident electron into a $^2\Pi_g$ antibonding orbital.

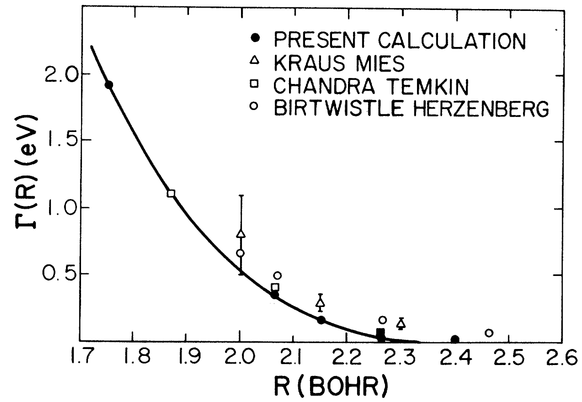

FIG. 2. Width of resonance as a function of internuclear distance in N_2.

The second ingredient of the theory is the determination of the vibrational eigenstates which describe the motion of the nuclei in each adiabatic electronic R-matrix level:

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + E_k(R) - E_{kq}\right] | \theta_{kq}\rangle = 0. \tag{3}$$

Equation (3) is a simple differential equation, completely decoupled from the electronic motion except for the potential energy $E_k(R)$. We have solved Eq. (3) variationally using an analytic basis set of Gaussian-type functions. By examining the Franck-Condon overlaps between the target- and compound-state vibrational levels one can already predict the possibility of significant vibrational excitation. In addition, by comparing the size of the adiabatic width with the spacing of the vibrational levels, E_{kq}, one immediately sees that there should be considerable substructure in the excitation cross sections. Although qualitatively these peaks should appear at the eigenvalues of Eq. (3) for the resonant R-matrix levels, the final details of the cross section depend critically on the interaction of the states with the external solutions.

The dynamical effects are simply condensed in the generalized vibrational R matrix, calculated as

$$\mathcal{R}_{vl,v'l'}{}^m = \sum_{k,q} \frac{\langle \chi_v | F_{kl}{}^m(a,R) | \theta_{kq}\rangle\langle\theta_{kq} | F_{kl'}{}^m(a,R) | \chi_{v'}\rangle}{E_{kq} - E} + \langle\chi_v | \mathcal{R}^{NR}(R) | \chi_{v'}\rangle. \tag{4}$$

The first sum includes explicitly the contribution of the 12 lowest vibrational levels, E_{kq}, associated with the first four electronic R-matrix states which obviously fully describe the resonance. The second term is simply the fixed-nuclei electronic R matrix with the lowest four electronic states removed. Since all our results include the Buttle correction, our overall expansion contains an infinite number of electronic levels. The final vibrational excitation cross sections are compared with the experimental results of Erhardt and Willmann,[3] Wong,[4] and Rohr[5] in Fig. 3 and the previous calculation of Chan-

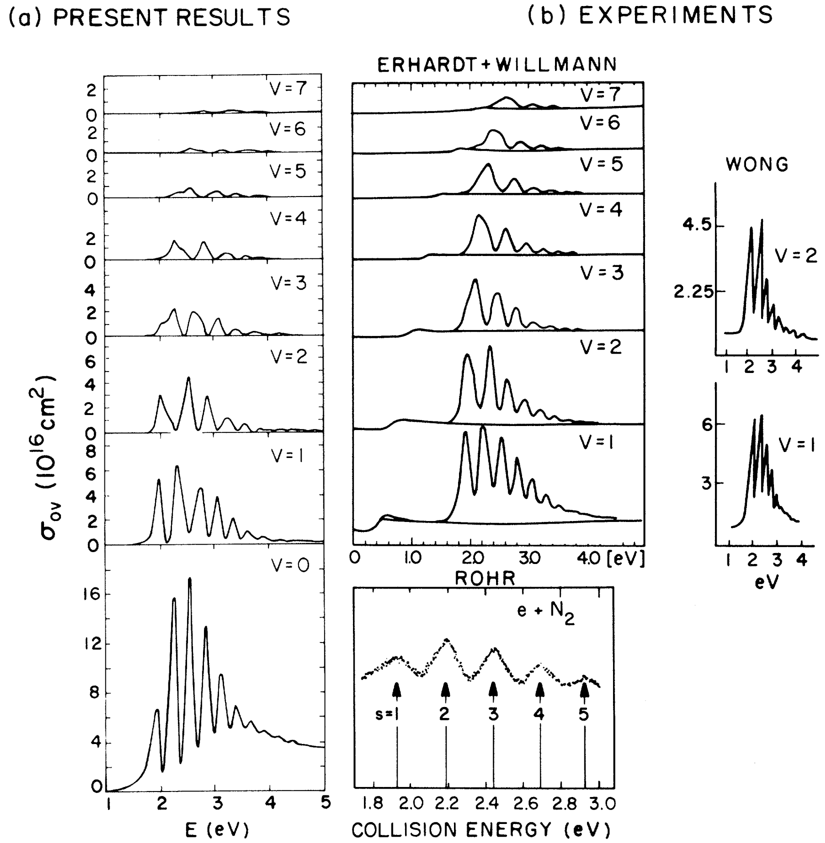

FIG. 3. Comparison of calculated and experimental vibrational excitation cross sections for N_2.

dra and Temkin[6] in Fig. 4. The present *ab initio* results are in good agreement as to the shapes and shifts of the experimental peaks with final vibrational quantum number and seem to confirm the quantitative normalization of Wong's latest experiment. The total cross section obtained by summing over all final vibrational quantum numbers appears to be about 10% larger than the experimental results of Golden[9] and Kennerly and Bonham.[10] The main features of the cross section are well represented and support the view of the authors that once the internal Born-Oppenheimer states of the compound system are known, a simple matching to known asymptotic states of the target will give correct results. The important interactions take place at short range where the appropriate frame of reference is the molecular or body frame. The vibrational close coupling suffers convergence difficulties by not recognizing the central role played by these internal basis states and expanding the scattering wave function in the asymptotic basis. This is especially true in a resonant collision where short-range correlations dominate the wave function. Once the Born-Oppenheimer states of the compound system are available, the rest is numerical quadrature.

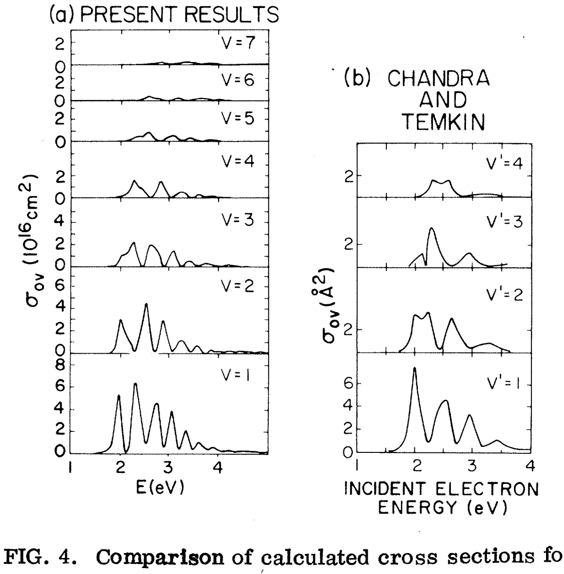

FIG. 4. Comparison of calculated cross sections for vibrational excitation in N_2.

In closing, it is worthwhile mentioning that the bulk of the computation involved in the present calculation concerned the determination of the electronic R-matrix levels at seven internuclear distances with use of already-existing fixed-nuclei R-matrix codes. The additional work to calculate the vibrational cross sections, which includes the fitting of the potential curves, determination of vibrational eigenstates and vibrational R matrices, and the final matching to the external solutions, was trivial because only two minutes of computing time on the CDC 6600 were needed to calculate the vibrational cross sections at over 100 energies. This enabled us to study the details of the transitions in a way which would be prohibitive with even the most efficient close-coupling technique.

Further details of the calculations will appear in later publications.

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[a] On sabbatical leave from the Los Alamos Scientific Laboratory, Los Alamos, N. M. 87545.

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Theory of Filament Formation in Self-Focusing Media

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The instability theory for sinusoidal perturbations is extended by use of an appropriate energy-conservation criterion. This theory predicts that perturbations initially grow exponentially but can subsequently either stabilize or decay depending on their transverse size.

In situations where intense laser beams traveling through nonlinear cubic media ($\epsilon=\epsilon_0+\epsilon_2|\vec{E}|^2$) result in multiple filament formation, there is a one-to-one correspondence[1] between the filaments and intensity spikes riding with the incident laser beams. Instability theories[2,3] that consider growth of intensity spikes or perturbations predict that they grow exponentially as long as the laser background is not appreciably depleted. Many important experimental facts concerning filament formation remain unexplained. These are stabilization of intensity in spikes (formation of stable waveguidelike filamentary tracks), existence of a well-defined threshold for filament formation, and an almost constant size of filaments in a given nonlinear medium. Some of these facts are adequately explained by the theory of filament formation presented here.

In our theoretical model, similar to that of Bespalov and Talanov,[2] we consider a complex perturbation (e_1+ie_2) riding on a uniform background laser optical field $|\vec{E}_0|$. Instead of assuming exponential growth we write the sinusoidal perturbation in the form[3,4]

$$e_{1,2}=e_{10,10}e^{\alpha(z)}\sin(K_{\perp x}x)\sin(K_{\perp y}y), \tag{1}$$

where $K_\perp^2=K_{\perp x}^2+K_{\perp y}^2$ relates to the characteristic size of the perturbation and $\alpha(z)$ is the growth parameter which is taken to be a real quantity.

Since both the background and the perturbation have infinite transverse extent, it is useful to consider cells of size $(\pi/K_{\perp x})\times(\pi/K_{\perp y})$ individually.[4] Overall conservation implies that energy in each "characteristic cell" should be conserved during propagation. According to Eq. (1) the energy of the perturbation, at distance z, in a char-

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