

Hybrid theory calculation of simultaneous vibration-rotation excitation in $e\text{-N}_2$ scattering

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Simultaneous vibration (v) and rotation (j) excitation of N_2 by electron impact is calculated in the hybrid theory from the relevant formulas (involving a -matrix elements previously calculated). All cross sections (labeled $v, j \rightarrow v', j'$) involving states with $v = 0, 1; 0 \leq j \leq 1; 0 \leq v' \leq 2; 0 \leq j' \leq 5$ have been evaluated. A representative sample of graphical results is presented. In particular, we find large discrepancies in magnitude from the partially phenomenological theory of J. C. Y. Chen.

We report here calculated results for simultaneous vibration-rotation electron-impact excitation of N_2 on the basis of the hybrid theory.¹ The basic formula for the differential cross section from a vibration-rotation¹ state v, j to v', j' is given by

$$\frac{d\sigma_{v'j';vj}}{d\Omega'} = \frac{k_{v'j'}}{k_{vj}} \frac{1}{4\pi} \sum_L A_L(v'j';vj) P_L(\cos\theta'), \quad (1)$$

where

$$A_L(v'j';vj) = (2L+1)(2j'+1) \times \sum (-1)^{l_j+\lambda_j+m+\mu} [(2l_i+1)(2\lambda_i+1)]^{1/2} a_{l_i l_j m}(v',v) a_{\lambda_i \lambda_j \mu}^*(v',v) \times \left(\begin{matrix} l_i & \lambda_i & L \\ 0 & 0 & 0 \end{matrix} \right) \left(\begin{matrix} l_j & \lambda_j & L \\ 0 & 0 & 0 \end{matrix} \right) \sum_J (-1)^J (2J+1) \left(\begin{matrix} l_i & l_j & J \\ m & -m & 0 \end{matrix} \right) \left(\begin{matrix} \lambda_i & \lambda_j & J \\ \mu & -\mu & 0 \end{matrix} \right) \left(\begin{matrix} j' & j & J \\ 0 & 0 & 0 \end{matrix} \right)^2 \left\{ \begin{matrix} l_i & \lambda_i & L \\ \lambda_j & l_j & J \end{matrix} \right\}. \quad (2)$$

The total cross section, which from (1) is seen to be proportional to A_0 , can conveniently be written in the form

$$\sigma_{v'j';vj} = \frac{k_{v'j'}}{k_{vj}} (2j'+1) \sum (-1)^J \frac{2J+1}{2l'+1} \left(\begin{matrix} j' & j & J \\ 0 & 0 & 0 \end{matrix} \right)^2 \left| \sum_m (-1)^m \left(\begin{matrix} l & l' & J \\ m & -m & 0 \end{matrix} \right) a_{ll'm}(v',v) \right|^2. \quad (3)$$

The idea of the hybrid theory¹ is to combine adiabatic-nuclei amplitudes for rotation with close-coupling amplitudes for vibration for any resonant partial wave (as in the Π_g case for $e\text{-N}_2$) which has a width narrower than the vibrational spacing but broader than the rotational spacing. Mathematically this amounts to replacing in Eq. (3) the adiabatic-nuclei elements (χ_v are target vibrational wave functions)

$$a_{l\lambda m}(v',v) = \int_0^\infty \chi_{v'}(R) a_{ll'm}(R) \chi_v(R) R^2 dR \quad (4)$$

by the elements $a_{v'l'm}^{(m)}$ coming from a close-coupling expansion in vibrational states of the wave function

$$\Psi^{(m)} = \Phi_R \sum_v F_v^{(m)}(\vec{r}) \chi_v(R), \quad (5)$$

where Φ_R is the electronic part of the target wave function (with nuclei fixed at a distance R apart), and the $F_v^{(m)}$, describing the scattered particle, are further decomposed into spherical components,

$$F_v^{(m)}(\vec{r}) = r^{-1} \sum_l f_{vl}^{(m)}(r) Y_{lm}(\Omega). \quad (6)$$

The asymptotic form of the solutions of the resulting coupled equations for $f_{vl}^{(m)}(r)$ then yields the elements $a_{v'l'm}^{(m)}$; the hybrid theory then substitutes them in place of $a_{l\lambda m}(v',v)$ in the relevant cross-section formulas.¹ For nonresonant partial waves one uses the $a_{l\lambda m}(v',v)$ calculated from Eq. (4), where on the right-hand side the $a_{l\lambda m}(R)$ are the fixed-nuclei amplitudes calculated with nuclei fixed at each distance R apart.

All the $a_{l\lambda m}(v',v)$ for nonresonant partial waves ($m=0 \rightarrow 5$, g , and u except Π_g) plus resonant

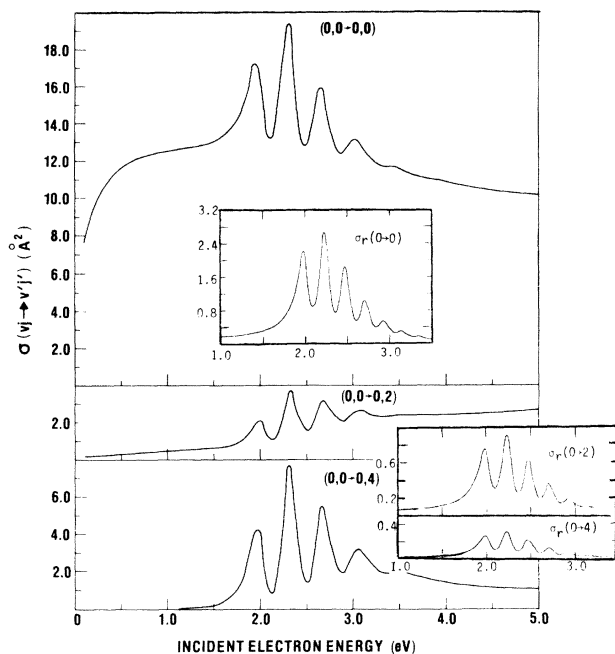


FIG. 1. Integrated cross sections ($v, j \rightarrow v', j'$) for vibrationally elastic ($v=v'=0$) with $j=0$ and even j' ($=0, 2, 4$). Insets are the results of Chen, Ref. 2. Higher j' cross sections are very small. Note nonmonotonicity in j' of present results as compared to Chen's. See text for further discussion of this and subsequent figures.

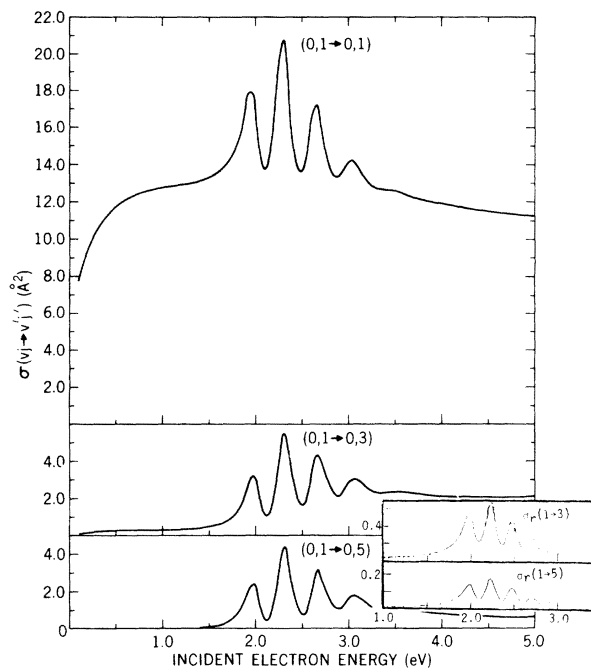


FIG. 2. Integrated cross sections for vibrationally elastic ($v=v'=0$), but between odd j, j' states ($j=1; j'=1, 3, 5$). Insets are from Chen, Ref. 2. Note monotonicity but difference in magnitude of respective theories.

($\Pi_g \Rightarrow m=1, g$) $\alpha_{v, j', v_l}^{(j)}$ were calculated previously¹; however, they were used only in simplified cross-section formulas derived by summing over final rotational quantum numbers (j') and averaging over initial j .

In this paper we have calculated the detailed simultaneous rotation-vibration cross-section formulas for low-lying v and j excitation and elastic scattering. Since the fixed-nuclei calculations showed only minute dependence on R for all non-

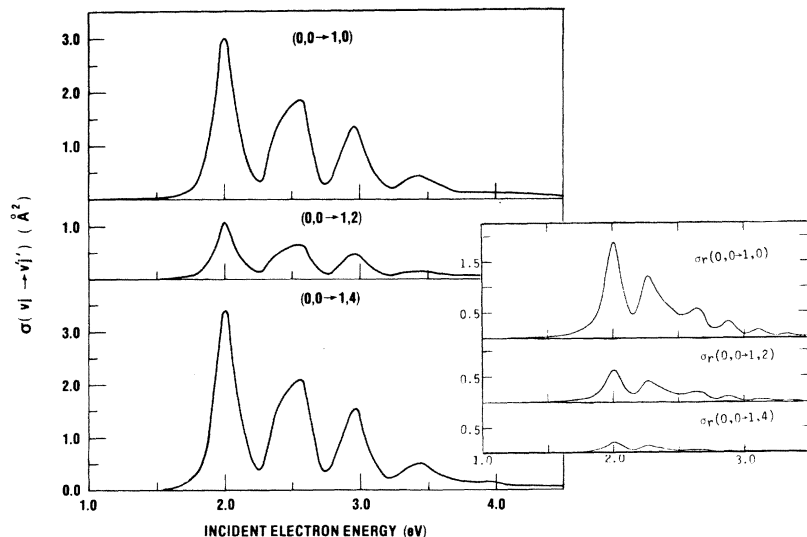


FIG. 3. Integrated cross sections for excitation of first vibrationally excited states, $v=0 \rightarrow v'=1; j, j'$ even. Insets from Chen, Ref. 2.

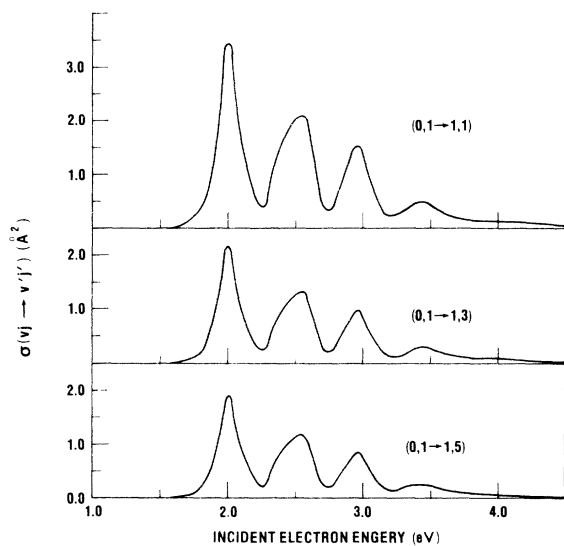


FIG. 4. Integrated cross section for $v = 0 \rightarrow 1$; j, j' odd.

resonant partial waves,¹ one can see from Eq. (4) that their contribution to all $v' \neq v$ transitions is very small. As a result, these (negligible) non-resonant contributions are not included in our $v' \neq v$ transitions.

Figures 1–6 show various total integrated cross sections. (First we remind the reader that oscillations in energy of all integrated cross sections come from the vibrational close-coupling part of the method for the resonant Π_g partial wave, as discussed in Ref. 1.) The following seem to be the most salient features: the various $(v, j \rightarrow v', j')$ transitions for which j and j' are *even* are such that the $j = 0 \rightarrow 2$ cross sections are consistently *smaller* than the $j = 0 \rightarrow 4$ transitions. This is true for all values of v and v' that we have calculated (cf. Figs. 1, 3, and 5). The result seems to be due to the specific way the vector coupling coefficients

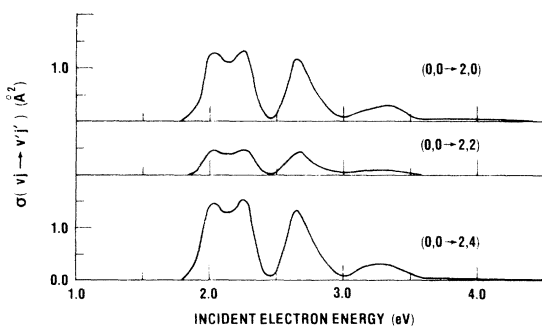


FIG. 5. Integrated cross sections for excitation of second vibrational state from ground state; j, j' even.

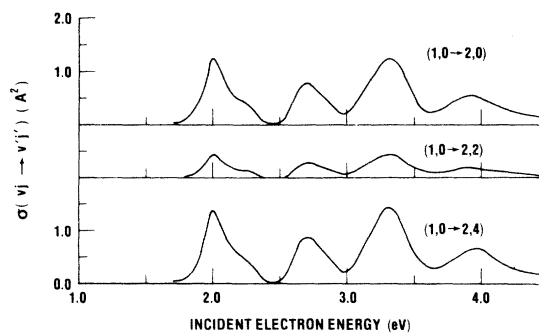


FIG. 6. Integrated cross sections for excitation of second vibrational level from first; j, j' even.

enter the simultaneous vibration-rotation formulas. When j and j' are odd (recall the selection rule, Δj even, for excitation with Σ electronic states of homonuclear molecules but *not* within higher electronic states³), then the $j = 1 \rightarrow j'$ decrease monotonically with j' (cf. Figs. 2 and 4).

These results are in sharp contrast to those of Chen.² He has calculated vibrational-rotational cross sections, as shown in the insets of Figs. 1–3. In the inset of Fig. 1, one sees a monotonic decrease of his cross sections. As shown in Fig. 2 Chen finds that the monotonicity persists, and

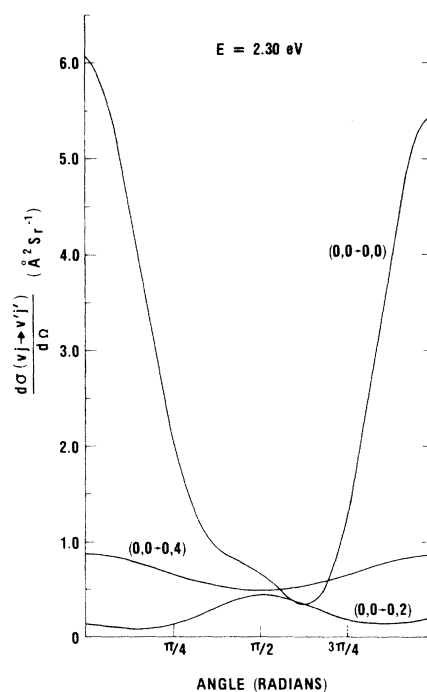


FIG. 7. Angular distributions for $v = v' = 0$ and j, j' even ($E = 2.3$ eV). Note forward and backward peaking of pure elastic, but similarity of all three around 90° .

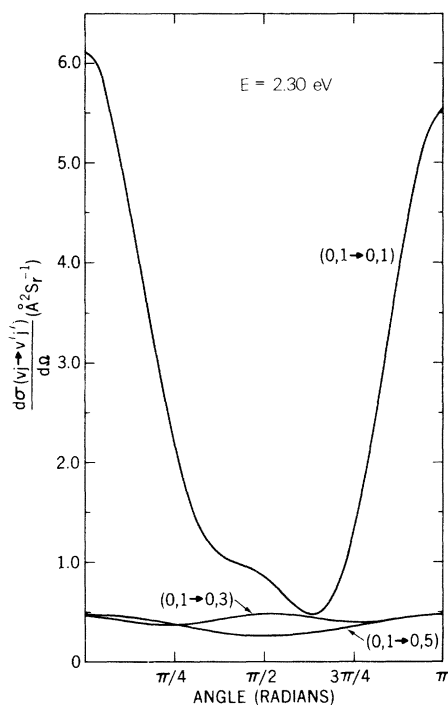


FIG. 8. Angular distribution for $v=0 \rightarrow 0$; j, j' odd ($E=2.3$ eV). Note similarity to even- j, j' results, with the exception that $j=1 \rightarrow 3$ is slightly larger than $j=1 \rightarrow 5$.

we find monotonicity in that case also; but note the difference in magnitude here as well as in Figs. 1 and Fig. 3.

Figures 7–12 give various angular distributions. Salient comments on these are included in the figure captions.

In assessing the comparative results of Chen and ourselves, the following points should be kept in

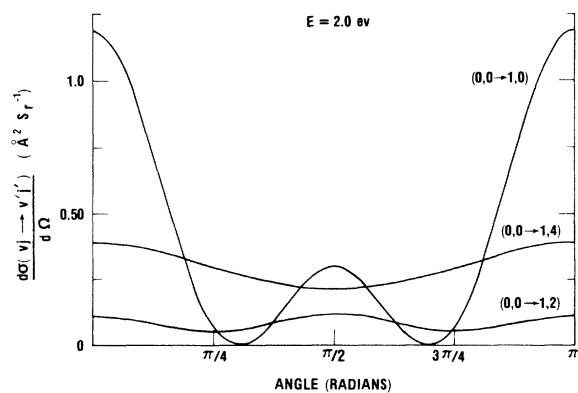


FIG. 9. Angular distribution for $v=0 \rightarrow 1$; j, j' even ($E=2$ eV). Note almost pure atomic d -wave character of $j'=0 \rightarrow 0$ cross section but not of others.

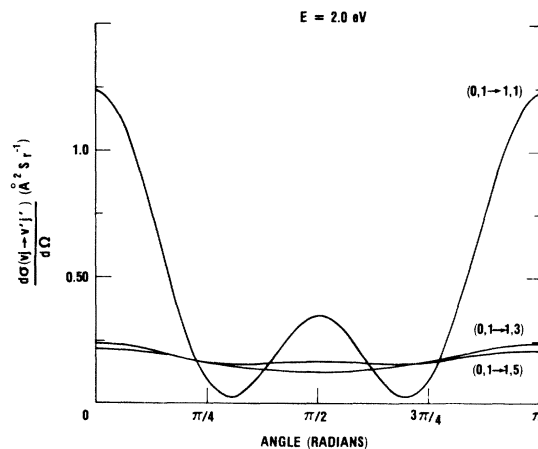


FIG. 10. Angular distribution for $v=0 \rightarrow 1$; j, j' odd ($E=2$ eV). Note d -wave character of rotationally diagonal cross section in this case also.

mind: First, his calculation was done before the most important recent developments were made in *ab initio* calculational theory of low-energy electron-molecule scattering.⁴ Second, his calculation refers to the resonant contribution only in such a way that it effectively factors between electronic and nuclear parts. The electronic factor was fitted to the magnitude $v=0 \rightarrow 1$ (rotationally averaged) cross section as it was then thought to obtain. The detailed resonant structure was then fitted by the nuclear factor calculation with appropriately chosen parameters. As a result of this factorization and parametrization, Chen's results do not depend explicitly on the electronic state (specifically the quantum numbers of the resonance partial wave of the scattered electron). This is clearly not the case in our detailed theory.

Under these circumstances, it is inappropriate to press comparisons with our calculation too far. The accuracy of our absolute cross sections has

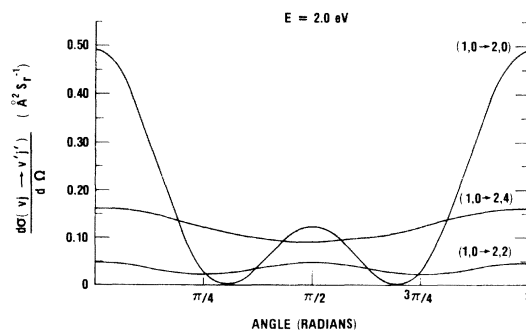


FIG. 11. Angular distribution for $v=1 \rightarrow 2$; j, j' even ($E=2$ eV). The d -wave character of rotationally diagonal cross section persists.

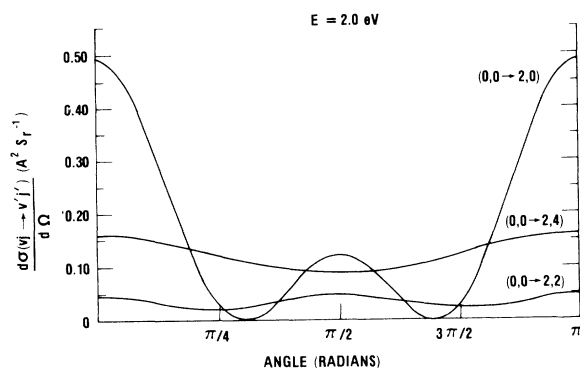


FIG. 12. Angular distribution for $v=0 \rightarrow 2$; j, j' even ($E=2$ eV).

been discussed in Ref. 1. To summarize in a form appropriate to the present results we would say that aside from purely elastic cross sections our results should be correct to better than a factor of 2. For purely elastic cross sections [i.e. the $(0,0 \rightarrow 0,0)$ and $(0,1 \rightarrow 0,1)$ cross sections of Figs. 1 and 2] we estimate an accuracy of 25%. [These esti-

mates are based on comparisons with experiment: for vibrational excitation (Fig. 14 of Ref. 1) the comparison is better than a factor of 2, and for total scattering (Fig. 7 of Ref. 1, of which the dominant part is pure elastic scattering) the calculation is within 25% of experiment.⁵ To this we argue further that the introduction of rotational degrees freedom via the adiabatic-nuclei approximation, whose validity may be cogently argued for¹ by virtue of $\Gamma(R) \gg \Delta E_{\text{rot}}$ for all relevant R , does not add measurably to these errors.] In addition, there are certainly inaccuracies in the detailed shape of the fine-structure features, as discussed in Ref. 1 (cf. in particular Fig. 14 of Ref. 1⁶).

For these reasons, therefore, it would clearly be desirable to have experimental results of at least some of these simultaneous rotation-vibration cross sections. However, these measurements are very difficult because of the small rotational spacing ($\sim 10^{-4}$ eV) of N_2 . Nevertheless, such measurements are underway in the laboratory of the late George Schulz at Yale.

We are grateful for the inspiration and encouragement provided us by the late Dr. George Schulz.

¹N. Chandra and A. Temkin, Phys. Rev. A **13**, 188 (1976).

²J. C. Y. Chen, Phys. Rev. **146**, 61 (1966), and references therein.

³A. Temkin and F. H. M. Faisal, Phys. Rev. A **3**, 520 (1971).

⁴For a review covering developments through 1971, see D. Golden, N. Lane, A. Temkin, and E. Gerjuoy, Rev. Mod. Phys. **43**, 642 (1971). For comments on develop-

ments since 1971 (particularly involving vibrational excitation), see A. Temkin, Comments At. Mol. Phys. (to be published).

⁵D. E. Golden, Phys. Rev. Lett. **17**, 847 (1966).

⁶We would like to reiterate footnote 36 of Ref. 1: We are preparing a NASA Technical Note with numerical values of vibrational cross sections in many cases of interest.