Internuclear dependence of the polarizability of N_2

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The dependence of the polarizabilities $\alpha_0(R)$ and $\alpha_2(R)$ [or equivalently $\alpha_\parallel(R)$, $\alpha_\perp(R)$] on the internuclear separation R has been synthesized for the N_2 molecule in its ground (Σ_g^+) state. The significance of this dependence for a previous calculation of e-N_2 vibrational excitation is indicated.

I. ANALYSIS AND RESULTS (REF. 1)

The dependence of the polarizability on internuclear separation is an important element of the theory of low-energy scattering of electrons from diatomic molecules. Specifically, matrix elements of the polarizability between vibrational states of N_2 play a vital role in the close coupling portion of the hybrid theory of e-N_2 vibrational excitation.[2] For N_2 as for any homonuclear target the polarization potential for large r, where r is the distance of the electron from the nuclei (assumed fixed), can be written (in atomic units)

$$V_{\text{pol}} = [\alpha_0(R) + \alpha_2(R)P_2(\cos\theta)]/2r^4 . \tag{1}$$

In Eq. (1) R is the internuclear separation and θ is the angle between the electron and the internuclear axis. In place of α_0 and α_2 one often uses the parallel ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) polarizabilities:

$$\begin{aligned} \alpha_\parallel(R) &= \alpha_0(R) + \alpha_2(R) , \\ \alpha_\perp(R) &= \alpha_0(R) - \tfrac{1}{2}\alpha_2(R) . \end{aligned} \tag{2}$$

We are concerned with the R dependence of these quantities [called collectively the polarizability $\alpha(R)$]. Specifically we shall synthesize a curve from values of $\alpha(R)$ at $R = 0$, $R = R_0$, and $R = \infty$ and the derivatives at $R = R_0$. In our original hybrid calculation[2] an internuclear dependence was linearly interpolated from the polarizabilities at the equilibrium separation $R_0 = 2.068$ and their values at $R = 0$, the united-atom limit, which in this case approaches silicon in the $^1D^e$ state of the ground configuration. Our original estimate of $\alpha_0(0)$ was in fact erroneous; a recent calculation of Reinisch and Meyer[3] gives for the ground $^3P^e$ state of Si

$$\alpha_{\text{Si}}(^3P^e) \cong 36a_0^3 . \tag{3a}$$

The ground state of silicon differs from the above noted $^1D^e$ of the united-atom limit, but both states being of the same configuration $[(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2]$, it can confidently be expected that none of these polarizations will differ

widely from one another; thus for the purposes of our fit we use

$$\alpha_0(0) = 36a_0^3 . \tag{3b}$$

As for $\alpha_2(0)$, since at $\alpha_\parallel = \alpha_\perp$ at $R = 0$, it follows from (2) that

$$\alpha_2(0) = 0 . \tag{3c}$$

At the equilibrium separation we use experimental values of Bridge and Buckingham[4]

$$\alpha_0(R_0) = 11.9a_0^3 , \tag{4a}$$

$$\alpha_2(R_0) = 3.13a_0^3 , \tag{4b}$$

the latter value differing somewhat from another one ($4.2a_0^3$) used in our original calculation, which in turn was taken from the fixed-nuclei calculation of Burke and Chandra.[5]

The most nontrivial of the conditions we shall use are the derivatives of the polarizabilities at $R = R_0$. The magnitude of $(d\alpha_0/dR)_{R_0} \equiv \alpha_0'(R_0)$ has been measured[6] to be

$$|\alpha_0'(R_0)| = 5.7a_0^2 . \tag{5}$$

Stansbury *et al.*[6] have argued on the basis of the polarizability of H_2 and its united limit, He(^1S), that the slope at $R = R_0$ should be positive. However, whereas H_2 has a larger polarizability than its united-atom limit $[(\alpha_0)_{H_2} = 5.5a_0^3; \ \alpha_{\text{He}} = 1.38a_0^3]$, the values for N_2 and Si, Eqs. (4a) and (3a), indicate the united limit has a much larger polarizability; thus one might, on the contrary, expect that the slope inferred from Stansbury *et al.*[6] should be negative!

A strong argument for a positive slope can be given using a perturbation theory going back to Kirkwood[7] as elaborated in a convenient form in Hirschfelder, Curtiss, and Bird.[8] They developed an approximate expression for polarizability involving expectation values of $\langle z^2 \rangle$ and $\langle x^2 \rangle$. We have used Nesbet's values[9] of these expectation values in the vicinity of R_0, and taking suitable differences, we find a value of $\alpha_0'(R_0)$ which is qualitatively in accord with the experimental val-

ue,[6] but more important it indicates that the sign
is positive. This method of estimating $\alpha_0'(R_0)$ was
taken over from Brandt *et al.*[10] who used it to
evaluate $\alpha_2'(R_0)$. They find a value of $\alpha_1'(R_0)$ which
using (2) implies

$$\alpha_2'(R_0) = 3.6a_0^2 . \tag{6}$$

Finally at $R = \infty$ the polarizability of N_2 is simply
that of two nitrogen atoms[11]

$$\lim_{R \to \infty} \alpha_0(R) = 2\alpha_N \simeq 15.3a_0^3 , \tag{7a}$$

whereas

$$\lim_{R \to \infty} \alpha_2(R) = 0 . \tag{7b}$$

Given these conditions it is easy to fit a curve to
$\alpha_2(R)$. With use of Eqs. (3b), (4b), and (7b) we
find a satisfactory curve for $\alpha_2(R)$ to be given by

$$\alpha_2(R) = 0.683R^3 \exp(-0.152R^2) . \tag{8}$$

For $\alpha_0(R)$ which is less trivial, we have used the
interpolation formula

$$\alpha_0(R) = A_1 + A_2 e^{-\sigma R} + A_3 \tan^{-1}R . \tag{9}$$

One finds Eqs. (3a), (4a), (5), and (7a) lead to four
satisfactory equations for A_1, A_2, A_3, and σ. In
Fig. 1 we plot the two resulting curves for $\alpha_0(R)$
corresponding to positive and negative values of
$\alpha_0'(R_0) = \pm 5.7$.

If $\alpha_0'(R_0)$ is positive, then it is easy to see that
the conditions specified for it demand that any
curve must have at least one minimum and one
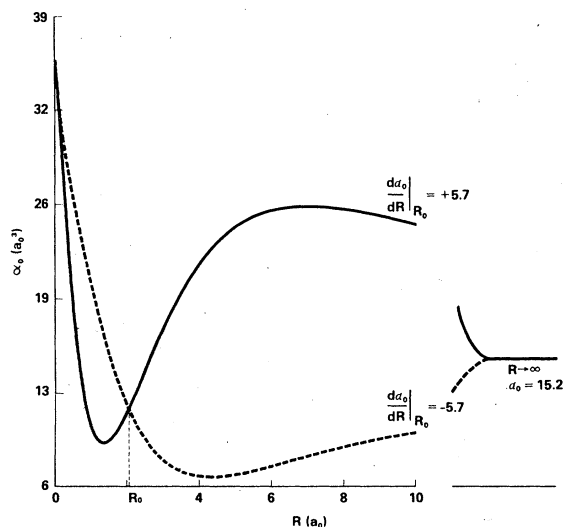maximum between $R = 0$ and $R \to \infty$. Our own curve

FIG. 1. $\alpha_0(R)$ for N_2 as determined by the conditions
specified in the text for positive and negative slope at
the equilibrium separation $R_0 = 2.016a_0$. The positive
slope curve is given by $\alpha_0(R) = 178.7 - 142.7$
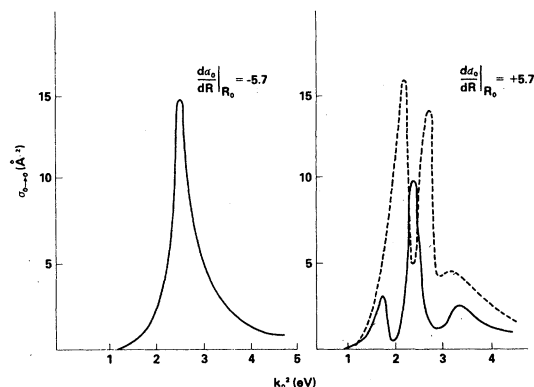$\times\exp(-0.50572R) - 104.0\tan^{-1}R$.

FIG. 2. Vibrationally elastic cross section as a func-
tion of incident electron energy in an eight-state calcu-
lation ($v = 0,1,2,3,4; l = 2,4$). Results only include the
Π_g partial wave. The left-hand results correspond to the
$\alpha_0(R)$ with negative slope in Fig. 1, and the right to the
$\alpha_0(R)$ with positive slope. Note only the right curve con-
tains substructure. The dashed curve represents the
results of our original calculation (Ref. 2) with the same
amount of coupling; note the difference in magnitude.

has just one such minimum and maximum; but
even so it is by no means a simple curve.

We have been able to provide a much more de-
finitive demonstration that the slope of $\alpha_0(R)$ at R_0
is positive by repeating the vibrational close coup-
ling portion (for the resonant Π_g partial wave) of
our hybrid theory e-N_2 calculation using the two
forms of $\alpha_0(R)$ pictured in Fig. 1. Results are
given in Figs. 2 and 3; as noted in the caption the
calculations do not correspond to a sufficient
amount of l and v coupling to yield convergence,
nevertheless, the absence of substructure in $\alpha_0'(R)$
$= -5.7$ curves and its presence for $\alpha_0'(R_0) = +5.7$
shows, without question, that the positive slope is
correct!

It is to be emphasized because of the rather *ad
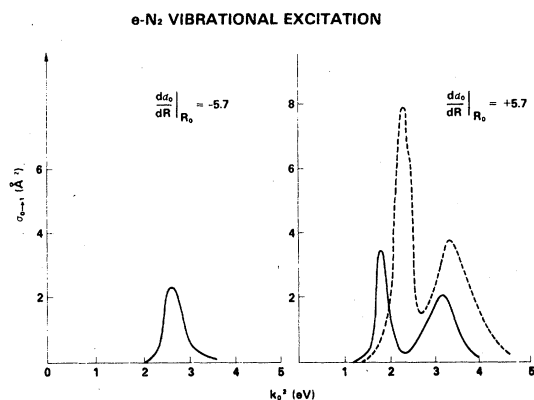hoc* form of our interpolation formulas, that these

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FIG. 3. Same as Fig. 2 for the excitation of the first
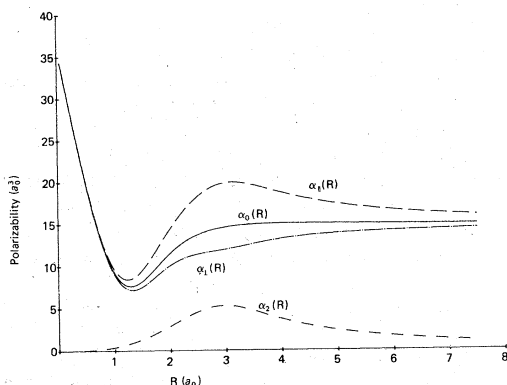· vibrational state.

FIG. 4. Final fits to the polarizabilities α (R) as defined in Eqs. (10) and (11). See note added in proof.

curves, $\alpha(R)$, may not be very accurate in a point for point sense as a function of R. (We shall call them synthetic curves.) However, we do believe they are sufficiently accurate for many applications including our own kind of scattering calculation.

Two final remarks are in order concerning our scattering calculations. Although as stated the number of states used does not constitute convergence, our experience is (cf. Figs. 1 and 2 of Ref. 2) that the magnitude of the peaks will not change very much from their converged values. This then suggests that the converged calculation may yield an approximate 40% diminution in the normalization of the vibrationally inelastic curves from those calculated in Ref. 1. [A complete calculation using the newer $\alpha_0(R)$ and $\alpha_2(R)$ with enough l and v coupling for effective convergence is underway in this laboratory.]

Secondly, although the excitation of the lower vibrational states is probably sensitive only to the slope and value of α in the neighborhood of R_0, it is expected that the excitation of more highly excited vibrational levels (which results are needed in many atmospheric applications) will rely more heavily on the full shape of the $\alpha(R)$ curves exemplified in Fig. 1.

II. CONCLUDING DISCUSSION

After this work was completed,[1] we received an unpublished report of Purvis[12] and very recently a preprint of Morrison and Hay,[13] both calculating, in the Hartree-Fock approximation, $\alpha_{\parallel}(R)$ and

$\alpha_{\perp}(R)$ in the vicinity of R_0. Their respective results are very close to each other and to the experimental static polarizabilities of Bridge and Buckingham[4] (<5%). However, their inferred derivative, $\alpha_0'(R_0) \cong 7a_0^2$, is somewhat further from the experimental value of the slope,[6] $\alpha_0'(R_0) = 5.7a_0^2$. Assuming the experimental result is reasonably accurate, we believe our $\alpha_0(R)$ may be more accurate than these calculations.

With regard to $\alpha_2(R)$, we cannot make such a claim, since the accuracy of the theoretical inference[10] of $\alpha_2'(R_0)$ given in Eq. (6) cannot be assessed. The calculated result of Purvis[12] and Morrison and Hay[13] [~5.5a_0^2] is larger than the value from Eq. (6) by about the same as obtains between their value of $\alpha_0'(R_0)$ and the experiment. However, that may be coincidence.

Note added in proof. Professor A. Dalgarno has kindly pointed out to us that it is not necessary for $\alpha_0(R)$ to have a maximum beyond R_0. Furthermore, we expect $\alpha_0(R)$ and $\alpha_2(R)$ to approach their asymptotic value in the same way (i.e., as the same inverse power of R). We have been able to provide new fits to these curves which essentially display these features:

$$\alpha_0(R) = A + Be^{-\gamma R} + C\,\frac{1 - e^{-\gamma R^3}}{R^2} \tag{10}$$

with $A = 15.3$, $B = 20.7$, $C = -44.8806$, and $\gamma = 0.524\,76$; and

$$\alpha_2(R) = D(1 - e^{-\mu R^5})/R^2 \tag{11}$$

with $D = 58.4841$ and $\mu = 0.52476$. In Fig. 4 we plot these curves together with the associated $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ from Eqs. (2). We would expect these curves to be more accurate than the fits in Eqs. (8) and (9), particularly for large R.

[1]This material was presented at the International Conference on the Physics of Electronic and Atomic Collisions satellite workshop "Five Problems in Electron-Molecule Collisions," Orsay, July 29, 1977 (unpublished).

[2]N. Chandra and A. Temkin, Phys. Rev. A 13, 188 (1976).

[3]E. A. Reinisch and W. Meyer, Phys. Rev. A 14, 915 (1976). The polarizability also depends on the M quantum number. The value calculated by Reinisch and Meyer are averaged over M values but again the averaging is not expected to have much effect (cf. text).

[4]N. J. Bridge and A. D. Buckingham, Proc. R. Soc. A 295, 334 (1966).

[5]P. G. Burke and N. Chandra, J. Phys. B 5, 1696 (1972).

[6]E. J. Stansbury, M. F. Crawford, and H. L. Walsh, Can. J. Phys. 31, 954 (1953).

[7]J. G. Kirkwood, Phys. Z. 33, 57 (1932).

[8]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 942 *et seq*.

[9]R. K. Nesbet, J. Chem. Phys. 40, 3619 (1964).

[10]M. A. Brandt, D. H. Truhlar, and F. A. Van-Catledge, J. Chem. Phys. 64, 4957 (1976). I would like to thank Dr. Truhlar for helpful correspondence on this methodology and these calculations for inferring the derivative of the polarizability.

[11]R. R. Teachout and R. T. Pack, Atomic Data 3, 195 (1971).

[12]G. W. Purvis, III (unpublished).

[13]M. A. Morrison and P. J. Hay, J. Phys. B 10, L647 (1977).