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# MEMORANDUM

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# INTERACTIONS BETWEEN GROUND-STATE NITROGEN ATOMS AND MOLECULES

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## SUMMARY

Potential-energy curves for nitrogen atom (N-N) interactions corresponding to the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$, B $^3\Pi_g$, C $^3\Pi_u$, and a $^1\Pi_g$ states of the nitrogen molecule $N_2$ as well as curves for the atom-molecules $(N\text{-}N_2)$ and molecule-molecule $(N_2\text{-}N_2)$ interactions have been calculated. All calculations have been based as nearly as possible on experimental data, including spectroscopically determined vibrational energy levels, scattering cross sections of atomic beams in gases, and measured vibrational relaxation times. In cases where experimental data were not available, approximate quantum-mechanical calculations have been made. Results obtained by these various methods are remarkably consistent with one another and are believed to have good accuracy.

## INTRODUCTION

The various possible interactions between ground-state nitrogen atoms and molecules are of interest in a number of connections, such as the calculation of the thermodynamic and transport properties of air at extremely high temperatures, the active nitrogen problem, and various upper atmospheric phenomena. Six potential-energy curves have to be considered, four of which arise when two ground-state nitrogen atoms come together (N-N). (See ref. 1.) The other two are the atom-molecule $(N\text{-}N_2)$ and molecule-molecule $(N_2\text{-}N_2)$ interactions, which are orientation dependent.

Three of the four types of N-N interactions, the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, and $^5\Sigma_g^+$, correspond to bound states, the last being only very weakly bound. The fourth state, the $^7\Sigma_u^+$, is repulsive. It is easy to obtain a major part of the potential curves for the X $^1\Sigma_g^+$ and the A $^3\Sigma_u^+$

states from available spectroscopic data by using the Ryberg-Klein-Rees (RKR) method (refs. 2 to 5). The only precise information on the ${}^5\Sigma_g^+$ state is that it causes predissociation in two bound excited states of $N_2$, the B ${}^3\Pi_g$ and the a ${}^1\Pi_g$ states. (The lines reported in ref. 6 as being due to a transition from ${}^5\Sigma_g^+$ to A ${}^3\Sigma_u^+$ have since been reported in a private communication from Dr. C. M. Herzfeld to be due to another cause.) Accurate potential curves for these two states can be determined by the RKR method and combined with the experimental data on the predissociation limits to yield two points on the curve for the ${}^5\Sigma_g^+$ state. It was possible to derive a Morse curve which should be a reasonable approximation to the true curve by combining these two points with the relation $r_e^2\omega_e$ = Constant for the different electronic states of the same molecule (ref. 1, p. 456). The repulsive potential curve for the ${}^7\Sigma_u^+$ state was calculated from a delta-function model (ref. 7). This was checked against a potential obtained from an analysis of scattering measurements (ref. 8) and with one obtained from an analysis, based on the Schwartz, Slawsky, and Herzfeld theory (refs. 9 to 12), of measurements of vibrational relaxation times in nitrogen.

Relationships among the X ${}^1\Sigma_g^+$, A ${}^3\Sigma_u^+$, ${}^5\Sigma_g^+$, and ${}^7\Sigma_u^+$ states can be obtained from a very simple discussion along the lines of conventional first-order valence bond theory (the approximation of perfect pairing) as in reference 13. These relationships permit the "tails" of the X ${}^1\Sigma_g^+$ and A ${}^3\Sigma_u^+$ curves to be calculated once the ${}^5\Sigma_g^+$ and ${}^7\Sigma_u^+$ curves are known. These tails join smoothly to the curves obtained from the spectroscopic data by the RKR method. The perfect-pairing approximation also leads to simple relationships involving nitrogen molecules, so that the $N$-$N_2$ and $N_2$-$N_2$ interactions could be built up from the results on the N-N interactions. The $N_2$-$N_2$ interactions so obtained are in good agreement, after averaging overall orientations, with average $N_2$-$N_2$ interactions already known from the molecular scattering measurements of reference 8 and from high-temperature gas-viscosity data of reference 14.

For the sake of completeness, results are included for the C ${}^3\Pi_u$ state of $N_2$. This is a bound state and was treated by the RKR method.

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# SYMBOLS

| | |
|---|---|
| a | constant |
| a' | average radius of outermost electronic orbit of isolated atom |
| a,b,c,d | lettering system for atoms in two nitrogen molecules |
| B | constant |
| c | velocity of light |
| c' | parameter in equation (11) |
| D | constant |
| d | bond length of molecule |
| $E_{v,J}$ | vibration-rotation energy |
| $\Delta E$ | energy transferred on collision from vibration to rotation |
| f | function of vibration-rotation energy |
| g | function of vibration-rotation energy |
| g' | strength of delta function |
| h | Planck's constant |
| I | ionization potential of atom |
| $I_H$ | ionization potential of hydrogen atom |
| J | rotational quantum number |
| $J_{ij}$ | exchange integral |
| i,j | x, y, or z orbitals; used as subscripts with integrals Q and J |
| k | Boltzmann's constant |
| m | mass of molecule |
| n | number of electrons in an atom; also, number of molecules per cubic centimeter in appendix A |
| Q | summation of $Q_{ij}$ integrals |

| | |
|---|---|
| $Q_{ij}$ | Coulomb integral |
| $R$ | distance between centers of mass of interacting molecules |
| $R_c$ | distance of closest approach of centers of mass of two molecules for most effective velocity $v_o^*$ |
| $r, r_2$ | internuclear separations |
| $r_c$ | distance of closest approach of centers of mass of two atoms for most effective velocity $v_o^*$ |
| $r_e$ | equilibrium internuclear separation |
| $r_{max}, r_{min}$ | maximum and minimum values of $r$, respectively, for a vibrating molecule |
| $T$ | absolute temperature |
| $T_e$ | energy difference between bottom of potential curve for state in question and that for $X\ {}^1\Sigma_g$ state |
| $V$ | potential energy |
| $V_{dis}$ | London dispersion energy |
| $V_i$ | energy of ith vibrational level |
| $V_o$ | constant |
| $V(R)$ | potential energy as a function of $R$ |
| $V(r)$ | potential energy as a function of $r$ |
| $V_{eff}(r)$ | effective potential energy for rotating molecule |
| $v$ | vibrational quantum number |
| $v_o^*$ | most effective velocity for deactivation |
| $W_i$ | defined by equation (6) |
| $X$ | defined by equation (A5) |
| $x, y, z$ | coordinate axes |
| $\alpha$ | constant |

| | |
|---|---|
| $\bar{\alpha}$ | average polarizability of an $N_2$ molecule |
| $\epsilon$ | depth of Van der Waals minimum; Lennard-Jones potential parameter in equation (A10) |
| $\theta,\theta',\theta_1,\theta_2$ | angles in coordinate system used; see figure 3 |
| $\mu$ | reduced mass |
| $\rho$ | separation between delta functions |
| $\tau$ | relaxation time |
| $\tau^*$ | defined by equation (A7) |
| $\omega,\omega x$ | constants |
| $\omega_e$ | vibrational constant for equilibrium internuclear separation |

## BOUND STATES OF $N_2$

The potential-energy curves for the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, B $^3\Pi_g$, a $^1\Pi_g$, and C $^3\Pi_u$ bound states of $N_2$ are easily and rapidly obtained by the RKR method. This is a semiclassical procedure for determining the two distances which correspond to the classical turning points of vibrational motion, and it has the great advantage that it makes use of the experimental energy levels themselves without any reference to empirical functions for representing the potential-energy curve. The classical turning points $r_{max}$ and $r_{min}$ are given by the expressions

$$r_{max} = \left[(f/g) + f^2\right]^{1/2} + f \tag{1}$$

$$r_{min} = \left[(f/g) + f^2\right]^{1/2} - f \tag{2}$$

where f and g are functions of the vibration-rotation energy levels. The expressions for f and g (ref. 4) are particularly simple if the vibration-rotation energy $E_{v,J}$ can be expressed as a quadratic in v:

$$E_{v,J} = \omega\left(v + \frac{1}{2}\right) - \omega x\left(v + \frac{1}{2}\right)^2 - \alpha\left(v + \frac{1}{2}\right)J(J + 1) + BJ(J + 1) + DJ^2(J + 1)^2 + \ldots \tag{3}$$

where v and J are the usual vibration-rotation quantum numbers and $\omega, \omega x$, $\alpha$, B, and D are constants. If $E_{v,J}$ cannot be represented over the experimental range by equation (3), it can be expressed as a quadratic over different regions so that the entire experimental range can be covered by a series of quadratics. In such cases the following expressions are obtained for f and g for the rotationless (J = 0) state (refs. 4 and 5):

$$f = (8\pi^2 \mu c/h)^{-1/2} \sum_{i=1}^{n} (\omega x)_i^{-1/2} \log_e W_i \tag{4}$$

$$g = (2\pi^2 \mu c/h)^{1/2} \sum_{i=1}^{n} \Bigg[\frac{1}{4} \alpha_i (\omega x)_i^{-1} \left(V_i^{1/2} - V_{i-1}^{1/2}\right) + (\omega x)_i^{-1/2} \left(2B_i - \alpha_i (\omega x)_i^{-1} \omega_i\right) \log_e W_i\Bigg] \tag{5}$$

where $\mu$ is the reduced mass, $V_i$ is the energy of the ith vibrational level, and

$$W_i = \left[\frac{\omega_i^2 - 4(\omega x)_i V_i}{\omega_i^2 - 4(\omega x)_i V_{i-1}}\right]^{1/2} \left[\frac{\omega_i - 2(\omega x)_i^{1/2} V_{i-1}^{1/2}}{\omega_i - 2(\omega x)_i^{1/2} V_i^{1/2}}\right] \tag{6}$$

In equations (4) to (6), g, V, $\omega$, $\omega x$, $\alpha$, and B are in (centimeters)$^{-1}$, f is in centimeters, and the energy zero is chosen so that V = 0 at the bottom of the potential curve.

Application of the RKR method to the X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, B $^3\Pi_g$, and a $^1\Pi_g$ states is straightforward as shown in reference 5 and the results are given in tables I(a) to I(d). The experimental data were obtained by Herzberg (ref. 1), Jevons (ref. 15), Pearse and Gaydon (ref. 16), and Mulliken (ref. 17). The C $^3\Pi_u$ state is strongly perturbed by another $^3\Pi_u$ state (ref. 17), and to obtain good accuracy from equations (4) to (6) it was necessary to interpolate some additional points corresponding to hypothetical energy levels. The interpolation was done graphically on a plot of $\Delta E_v = E_{v+1,0} - E_{v,0}$ against v. The final results for the C $^3\Pi_u$ state are given in table I(e).

## $^5\Sigma_g^+$ STATE OF $N_2$

Although the $^5\Sigma_g^+$ state of $N_2$ is a bound state, it is considered separately because the binding is so weak that the state itself apparently has never been observed directly, and different methods are required for determining its potential-energy curve. The B $^3\Pi_g$ and the a $^1\Pi_g$ states of $N_2$ are both predissociated by the $^5\Sigma_g^+$ state (refs. 18 to 20), so that two points on the potential curve for the $^5\Sigma_g^+$ state can be determined from the predissociation limits. These limits are 80,003 ± 50 $cm^{-1}$ for $13 \leqq J \leqq 14$ for the a $^1\Pi_g$ state and 80,559 ± 50 $cm^{-1}$ for $J = 33$ for the B $^3\Pi_g$ state, where the zero of energy is taken as the minimum of the X $^1\Sigma_g^+$ state.

In a rotating molecule the effective potential energy is increased by addition of a centrifugal potential term equal to the kinetic energy of rotation (ref. 1, p. 426). Thus,

$$V_{eff}(r) = V(r) + \frac{hJ(J + 1)}{8\pi\mu cr^2} \tag{7}$$

where $V_{eff}(r)$ is the effective potential energy for the rotating molecule. (The notation $V(r)$ means "V as a function of r.") In predissociation a radiationless transition occurs at the point where two $V_{eff}(r)$ curves cross and follows Kronig's selection rules (ref. 1, p. 416) so that $\Delta J = 0$. Thus predissociation data give directly the crossing points of $V_{eff}(r)$ curves, and these must be translated back into crossings of curves for rotationless states according to equation (7). For the B $^3\Pi_g$ state, $V_{eff}(r)$ was constructed with $J = 33$ and $V(r)$ as given by V in table I(c). From this curve the intersection point of the B $^3\Pi_g$ and $^5\Sigma_g^+$ curves could be obtained by simply reading off that value of r for which $V_{eff}(r) = 80{,}559$ $cm^{-1}$. This procedure gave $r = 1.607$ angstroms which corresponds to an energy of 79,512 $cm^{-1}$ on the potential curve for the nonrotating molecule. The same procedure was used to find the intersection point of the a $^1\Pi_g$ and $^5\Sigma_g^+$ curves, using $J = 13.5$ and the data in table I(d). For the nonrotating molecule the intersection occurs at $r = 1.471$ angstroms and an energy of 79,711 $cm^{-1}$.

Since only two points are known on the $^5\Sigma_g^+$ curve, another relation is needed to determine the parameters of a Morse curve. The relation $r_e^2\omega_e = 2.598 \times 10^{-13}$ cm has been chosen (ref. 1, p. 456), which gives an average deviation of 4.8 percent for the other bound states of $N_2$. The only Morse curve which satisfies these three conditions and still has a reasonable dissociation energy is

$$V(r) + 744 = 744\left[1 - e^{-13.3(r-1.518)}\right]^2 \text{cm}^{-1} \tag{8}$$

where r is in angstroms and the zero of energy is taken to be two ground-state N atoms at infinite separation. Some uncertainty arises in equation (8) from the ±50 $\text{cm}^{-1}$ uncertainty in the predissociation limits as well as from the use of an empirical rule, but nevertheless this equation is probably the best approximation possible on the basis of the available data. The significant thing about the interaction energy is that it is practically zero over most of the separation range. Hence, on the average, there is practically no interaction in 5 out of 16 N atom collisions; this will have a significant effect on the calculation of the transport properties of nitrogen at high temperatures.

## $^7\Sigma_u^+$ STATE OF $N_2$

In reference 7 a method was given for calculating short-range intermolecular forces by means of a very simple model in which the nuclear Coulomb potentials are replaced by square wells which are allowed to degenerate into delta functions. The delta-function model was applied to the unstable b $^3\Sigma_u^+$ state of $H_2$ and to interactions between rare gas atoms for which no chemical bonding can occur. Despite the extreme simplicity of the model, the results were generally in better agreement with experiment than were results obtained by the very laborious standard quantum-mechanical approximations. On the basis of this model it is therefore easy to calculate the energy of the $^7\Sigma_u^+$ state of $N_2$, in which all the valence electrons are unpaired.

In the delta-function model the potential well for an electron in the field of a nucleus is replaced by a delta function of strength g', and in addition the electronic atomic orbitals are allowed to "float" around their original nuclei. The floating of the orbitals is achieved by allowing the delta functions to shift off the nuclei, so that the separation between the delta functions ρ is not necessarily equal to the internuclear separation r. For homonuclear interactions in which no chemical bonding occurs, the interaction energy V(r) is

$$V(r) = n(g')^2 e^{-c'\rho} \tag{9}$$

$$g' = 2^{1/2}(I/I_H) \tag{10}$$

where $n$ is the number of electrons in an atom, $I$ is the ionization potential of the atom, and $I_H$ is the ionization potential of a hydrogen atom. The parameter $c'$ is given in the equation

$$c' = g'\left(1 - e^{-c'\rho}\right) \tag{11}$$

The dependence of $\rho$ on $r$ is taken to be

$$\rho = r + 2a'e^{-r/a'} \tag{12}$$

where $a'$ is the average radius of the outermost electronic orbit of an isolated atom. Equations (9) to (12) together determine the potential energy as a function of $r$ when no bonding occurs.

For nitrogen the quantities needed to calculate $V(r)$ for the $^7\Sigma_u^+$ state are: $n = 7$, $I = 14.545$ electron volt (ref. 21), and $a = 0.56$ angstroms (ref. 22). Substitution of these values into equations (9) to (12) yields a potential energy which can be represented by

$$V(r) = 317.8\ e^{-2.753r}\text{ev} \qquad 1.3A < r < 3.2A \tag{13}$$

This potential is plotted in figure 1 together with a potential obtained from vibrational relaxation time measurements in $N_2$ (see appendix A) and a potential obtained indirectly from neutral atom beam scattering measurements (ref. 8). The relations used to obtain the $^7\Sigma_u^+$ curve from such measurements are given in the following sections. The agreement shown in figure 1 is within the uncertainties associated with the measurements and their theoretical interpretation.

## RELATIONS AMONG STATES OF $N_2$

A number of approximate but very useful relations among the different potential-energy curves of nitrogen can be obtained from the perfect-pairing approximation of simple valence bond theory (ref. 13). Consider the interaction between two nitrogen atoms in their $^4S$ ground states. As the two atoms approach, they can follow any one of the four interaction curves corresponding to the molecular states X $^1\Sigma_g^+$, A $^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$. It is easy to understand in a simple way how these four curves arise. The electron configuration of a $^4S$ nitrogen atom is $(1s)^2(2s)^2(2p_x)(2p_y)(2p_z)$, with three unpaired electrons in the p-orbitals. When two such atoms approach, these three electrons on each atom can be paired together in various ways. If all three are paired (i.e., the electron spins are antiparallel), the X $^1\Sigma_g^+$ ground state of $N_2$ results. If two electrons of one atom are paired with two of the other atom and the third electron is unpaired, the A $^3\Sigma_u^+$ state results, and so on, until the $^7\Sigma_u^+$ state of highest energy results from all the p-electrons being unpaired.

The mathematical expression of these statements is usually called the approximation of perfect pairing and is written as follows:

$$V = \underset{\text{all } i,j}{\Sigma Q_{ij}} \quad + \quad \underset{\substack{\text{orbitals with}\\ \text{paired spins}}}{\Sigma J_{ij}} \quad - \quad \frac{1}{2}\underset{\substack{\text{orbitals with}\\ \text{unpaired spins}}}{\Sigma J_{ij}} \quad - \quad \underset{\substack{\text{orbitals with}\\ \text{parallel spins}}}{\Sigma J_{ij}} \tag{14}$$

where $Q_{ij}$ is a Coulomb integral between the orbitals $i$ and $j$ and $J_{ij}$ is an exchange integral. The approximate expressions for the interaction energies of the four states of $N_2$ are thus

$$V(^1\Sigma) = Q + J_{xx} + J_{yy} + J_{zz} = Q + J_{xx} + 2J_{yy} \tag{15}$$

$$V(^3\Sigma) = Q + J_{xx} + J_{yy} - J_{zz} = Q + J_{xx} \tag{16}$$

$$V(^5\Sigma) = Q + J_{xx} - J_{yy} - J_{zz} = Q + J_{xx} - 2J_{yy} \tag{17}$$

$$V(^7\Sigma) = Q - J_{xx} - J_{yy} - J_{zz} = Q - J_{xx} - 2J_{yy} \tag{18}$$

where only the p-electrons are considered and $Q$ represents the summation of the $Q_{ij}$ integrals. Here the x-axis is chosen to coincide with the internuclear axis, and by symmetry $J_{zz} = J_{yy} \neq J_{xx}$. The following relations are readily obtained from equations (15) to (18):

$$V(^3\Sigma) = \frac{1}{2}\left[V(^1\Sigma) + V(^5\Sigma)\right] \tag{19}$$

$$V(^1\Sigma) = -V(^7\Sigma) + 2Q \approx -V(^7\Sigma) \tag{20}$$

In equation (20) use has been made of the fact that at large internuclear separations the coulombic interaction $Q$ between neutral atoms is very small. Equations (19) and (20) are probably fairly reliable since the approximation of perfect pairing has been used to obtain relations among the energies of the different states and not to calculate the energies themselves. These relations are extremely useful in the present case since the long-range tails for the X $^1\Sigma_g^+$ and A $^3\Sigma_u^+$ states are easily obtained from the potential-energy functions for the $^5\Sigma_g^+$ and $^7\Sigma_u^+$ states as given by equations (8) and (13).

In figure 2 are plotted the calculated potential-energy curves for the various states of $N_2$ relative to the minimum of the X $^1\Sigma_g^+$ curve as zero. The broken lines representing parts of the curves for the X $^1\Sigma_g^+$ and A $^3\Sigma_u^+$ states were calculated from equations (19) and (20) and join remarkably well with the solid lines calculated from spectroscopic data by the RKR method.

## $N$-$N_2$ AND $N_2$-$N_2$ INTERACTIONS

The results of the preceding section make it possible to calculate approximate potential curves for the $N$-$N_2$ and $N_2$-$N_2$ interactions. In the first place it is evident from equation (14) that both the $N$-$N_2$ and the $N_2$-$N_2$ interaction energies are the sums of the interactions between the atoms of the different molecules. Secondly, the interaction energy between an N atom which is part of an $N_2$ molecule and another N atom, either free or part of some other molecule, is approximately

$$V(NN) = Q - \frac{1}{2} J_{xx} - \frac{1}{2} J_{yy} - \frac{1}{2} J_{zz} = \frac{1}{2} V(^7\Sigma) + \frac{1}{2} Q \qquad (21)$$

in which only the valence p-electrons are considered. At fairly large internuclear separations, such as occur in ordinary thermal collisions even at very high temperatures, the coulombic term Q in equation (21) can be neglected. The curves for $V(^7\Sigma)$ which were plotted in figure 1 as derived from scattering measurements and from vibrational relaxation time measurements were calculated from equation (21) with $Q = 0$, since the measurements essentially determine $V(NN)$ rather than $V(^7\Sigma)$.

Since $V(^7\Sigma)$ is known from equation (13), it is simple to calculate $V(NN)$ from equation (21) and then obtain the $N$-$N_2$ and $N_2$-$N_2$ interactions by simply adding all the pertinent NN interactions. For example, the interaction between a molecule ab and a molecule cd would be written

$$V = V(r_{ac}) + V(r_{ad}) + V(r_{bc}) + V(r_{bd}) \tag{22}$$

where each of the terms on the right is given by equations (13) and (21), and the dependence of $V$ on orientation is given implicitly by the dependence of $r_{ac}$, $r_{ad}$, etc. on the molecular orientation.

For comparison with other results or for calculation of bulk properties it is frequently convenient to have the total interaction energy averaged over all orientations. The method of averaging and the assumptions involved have been discussed in detail in reference 8 for the case where the atom-atom interactions can be represented by an inverse power law. In the present case the atom-atom interactions are given by equations (13) and (21) in the form of an exponential, which can be written as follows:

$$V_r = V_0 e^{-ar} \tag{23}$$

where $V_0$ and $a$ are constants. To carry out the averaging, the coordinate system shown in figure 3 is convenient, in which $r$ is an atom-atom distance, $R$ is the distance between the centers of mass of the interacting molecules, and $d$ is the bond length of a molecule. Thus the $N\text{-}N_2$ interaction is given as

$$\langle V(R) \rangle = \frac{1}{4\pi} \int_0^{\pi} 2V_0 e^{-ar} 2\pi \sin\theta \, d\theta \tag{24}$$

where

$$r^2 = R^2 + (d/2)^2 - Rd \cos\theta \tag{25}$$

and $R$ is held fixed. If the integration variable is changed from $\theta$ to $r$, the integration is straightforward and yields

$$\langle V(R) \rangle = 2V_0 e^{-aR} (a^2 Rd)^{-1} \left[2(aR + 1)\sinh(ad/2) - 2(ad/2)\cosh(ad/2)\right] \tag{26}$$

The range of validity of $\langle V(R) \rangle$ in terms of $R$ evidently depends on the range of validity of $V(r)$ in terms of $r$. A plausible procedure for finding the range of $R$ is to hold $r$ fixed and average $R$ over all values of $\theta'$, so that

$$\langle R \rangle = r\left[1 + \frac{1}{12}\left(\frac{d}{r}\right)^2\right] \tag{27}$$

This is the desired relation between the limits of validity of $R$ and the limits of $r$ for the $N\text{-}N_2$ interaction.

The average $N_2\text{-}N_2$ potential is obtained in a similar manner.

$$\langle V(R)\rangle = \frac{1}{(4\pi)^2}\int_0^{\pi} 2\pi \sin\theta_1\, d\theta_1 \int_0^{\pi} 4V_0 e^{-ar_2^2} 2\pi \sin\theta_2\, d\theta_2 \tag{28}$$

in terms of the molecule-molecule coordinate system of figure 3. The integration goes smoothly to yield

$$\langle V(R)\rangle = 4V_0 e^{-aR}\left(a^3Rd^2\right)^{-1}\left[2(aR + 2)(\cosh ad - 1) - 2ad \sinh ad\right] \tag{29}$$

The range of validity is found by holding $r_2$ fixed and averaging over all values of $\theta'_1$ and $\theta'_2$, so that

$$\langle R\rangle = r_2\left[1 + \frac{1}{6}\left(\frac{d}{r_2}\right)^2\right] \tag{30}$$

The results for the average $N\text{-}N_2$ interaction can be represented by the equation

$$\langle V\rangle = 387.8\ e^{-2.733R}\,\text{ev} \qquad 1.5\text{A} < R < 3.2\text{A} \tag{31}$$

and the results for the average $N_2\text{-}N_2$ interaction by

$$\langle V\rangle = 826.4\ e^{-2.665R}\,\text{ev} \qquad 1.5\text{A} < R < 3.2\text{A} \tag{32}$$

Equations (31) and (32) were obtained by averaging the results from equations (13) and (21). Only equation (32) can be compared with similar potentials derived from other sources, and figure 4 gives such a comparison with average potentials derived from scattering measurements (ref. 8) and from high-temperature viscosity data (ref. 14). Since equation (32) is the result of essentially only a first-order perturbation calculation, it is of interest to add the second-order perturbation energy, the London dispersion energy, which is given approximately by the expression (ref. 23)

$$\langle V_{dis}\rangle = -\frac{3}{4}\frac{\bar{\alpha}^2 I}{R^6} = -\frac{36.0}{R^6}\ \text{ev} \tag{33}$$

for $R$ in angstroms, where $\bar{\alpha}$ is the average polarizability of an $N_2$ molecule and $I$ the ionization potential. The sum of equations (32) and (33) is also shown in figure 4. The agreement is certainly all that could be desired and is probably better than would have been expected in view of the various approximations made.

## CONCLUDING REMARKS

Potential-energy curves for interactions between ground-state N atoms have been calculated, as well as curves for the $N-N_2$ and $N_2-N_2$ interactions. Calculations have been based on experimental data whenever possible, and on approximate quantum-mechanical calculations when experimental data were unavailable. The interactions corresponding to the X $^1\Sigma_g^+$ ground state of $N_2$ are given by table I(a) and equations (20) and (13), the A $^3\Sigma_u^+$ state by table I(b) and equations (19) and (8), the $^5\Sigma_g^+$ state by equation (8), and the $^7\Sigma_u^+$ state by equation (13). Both the $N-N_2$ and the $N_2-N_2$ interactions are given as a function of orientation implicitly by equations (13), (21), and (22), and the interactions averaged over all orientations are given by equations (31) to (33). Portions of curves corresponding to interactions involving excited N atoms (the B $^3\Pi_g$, a $^1\Pi_g$, and C $^3\Pi_u$ states of $N_2$) are also given in the tables.

The results obtained by the different methods are remarkably consistent with one another. The results are also consistent with interactions calculated from data on scattering of atomic beams, high temperature gas viscosity, and vibrational relaxation times, as shown in the figures. This high degree of consistency gives confidence in the absolute accuracy of the results.

University of Maryland,
College Park, Md., May 1, 1958.

# APPENDIX A

## CALCULATION OF V(N . . . N) FROM VIBRATIONAL RELAXATION TIMES

Schwartz, Slawsky, and Herzfeld (ref. 9) have developed a theory which expresses the vibrational relaxation times of gases in terms of the molecular parameters of the system. Although a number of approximations and uncertainties exist in the theory, it is often capable of giving order-of-magnitude agreement with experiment. For diatomic gases the important collisions are the end-to-end ones, and the total potential is assumed to be composed of atom-atom potentials of the form

$$V = V_0 e^{-ar} - \epsilon \tag{A1}$$

where $V_0$ and $a$ are constants, $r$ is an atom-atom distance, and $\epsilon$ is the depth of the Van der Waals minimum. It is further assumed that in end-to-end collisions all interactions are negligible except the one between nearest atoms, so that equation (A1) represents the total potential if $r$ is interpreted as the nearest atom-atom distance and $\epsilon$ as the depth of the minimum for the molecule-molecule interaction. On this basis the following expression for the relaxation time $\tau$ has been obtained (refs. 9 to 12):

$$\tau\left(1 - e^{-\Delta E/kT}\right) = \frac{1}{4n}\left(\frac{\pi m}{2kT}\right)^{1/2} \frac{1}{Q_{el}P_{10}} \tag{A2}$$

where

$$Q_{el}P_{10} = \frac{8R_c{}^2}{3}\left(\frac{\pi}{3}\right)^{3/2} V_{10}{}^2\left(\frac{4\pi^3 m\ \Delta E}{a^2h^2}\right)^2 X^{1/2}\exp\left(-3X + \frac{\Delta E}{2kT} + \frac{\epsilon}{kT}\right) \tag{A3}$$

$$V_{10}{}^2 = \frac{a^2h^2}{8\pi^2 m\ \Delta E} \tag{A4}$$

$$X = \left[\frac{\pi^4 m(\Delta E)^2}{a^2 h^2 kT}\right]^{1/3} \tag{A5}$$

In the above expressions $n$ is the number of molecules per cubic centimeter, $m$ is the mass of a molecule, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $h$ is Planck's constant, $\Delta E$ is the energy transferred on collision from vibration to translation, and $R_c$ is the distance of closest approach of the centers of mass of two molecules for the "most effective" velocity for deactivation $v_o^*$ given by the expression

$$\begin{aligned} \frac{1}{2}\mu\left(v_o^*\right)^2 &= XkT \\ &= V_o \epsilon^{-ar_c} \end{aligned} \tag{A6}$$

where $\mu$ is the reduced mass of one molecule and $r_c$ is the atom-atom distance corresponding to $R_c$.

Equation (A2) can be written in the form

$$\begin{aligned} \tau^* &\equiv \tau_o\left[e^{\epsilon/kT} T^{-2/3} \sinh(\Delta E/2kT)\right] \\ &= C_1 e^{C_2/T^{1/3}} \end{aligned} \tag{A7}$$

where $\tau_o$ is the value of $\tau$ at some standard pressure and

$$C_1 = \frac{3}{128\pi^5}\left(\frac{3}{m}\right)^{1/2} \frac{h^2 k^{2/3} a^2}{p\ \Delta E R_c{}^2}\left[\frac{a^2 h^2}{\pi^4 m(\Delta E)^2}\right]^{1/6} \tag{A8}$$

$$C_2 = 3\left[\frac{\pi^4 m(\Delta E)^2}{a^2 h^2 k}\right]^{1/3} \tag{A9}$$

where $p$ is the standard pressure in dynes/cm$^2$. In equations (A7) to (A9), $C_2$ is a constant and $C_1$ is nearly constant except for values of $R_c$, which is weakly temperature dependent.

A plot of $\log_e \tau^*$ against $T^{-1/3}$ for the measurements of Blackman (ref. 24) and Lukasik and Young (ref. 25) gives a straight line as predicted by equation (A7). The slope of the line determines the parameter a in the potential function of equation (A1) as $a = 7.42$ per angstrom. The second parameter $V_0$ was determined from the condition that when $r + d = R = \sigma$, then $V = 0$, so that equation (A1) becomes

$$V_0 = \epsilon e^{a(\sigma-d)} \tag{A10}$$

where $d = 1.094$ angstroms is the bond length of $N_2$ (ref. 1, p. 553), and $\epsilon$ and $\sigma$ are taken as Lennard-Jones potential parameters for nitrogen molecules, which are $\epsilon/k = 79.8^\circ$ K and $\sigma = 3.749$ angstroms as determined from gas data (ref. 23, p. 1111).

The final potential between two N atoms of different molecules is thus found to be

$$V(NN) = (2.47 \times 10^6)e^{-7.42r} \text{ ev} \quad 1.9A < r < 2.1A \tag{A11}$$

where the range of validity of r was estimated from the highest and lowest experimental temperatures by means of equation (A6). This potential was converted by equation (21) to $V(^7\Sigma)$, the potential between two free N atoms, and was plotted in figure 1 for comparison with the potentials determined from the delta-function model and from scattering experiments. It is seen that equation (A11) is in approximate agreement with the other potentials, but is much steeper (ref. 26). This is a basic defect of the theory which has been pointed out previously. In view of the approximate nature of the theory of vibrational deactivation, the agreement shown in figure 1 is really surprisingly good.

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## TABLE I.- POTENTIAL ENERGY OF STATES OF $N_2$

[As far as the authors could determine, band-origin data were not available for most transitions involving A $^3\Sigma_u^+$, B $^3\Pi_g$, C $^3\Pi_u$, and a $^1\Pi_g$ states. Hence, band-head data were used and reported levels may be slightly in error.]

### (a) X $^1\Sigma_g^+$ state

| v | V, cm$^{-1}$ | V, electron volts | $r_{max}$, A | $r_{min}$, A |
|---|---|---|---|---|
| 0 | 1,175 | 0.1457 | 1.146 | 1.055 |
| 1 | 3,505 | .4346 | 1.185 | 1.027 |
| 2 | 5,806 | .7199 | 1.213 | 1.008 |
| 3 | 8,079 | 1.002 | 1.238 | .994 |
| 4 | 10,323 | 1.280 | 1.261 | .983 |
| 5 | 12,538 | 1.555 | 1.282 | .973 |
| 6 | 14,725 | 1.826 | 1.302 | .964 |
| 7 | 16,882 | 2.093 | 1.321 | .956 |
| 8 | 19,011 | 2.357 | 1.339 | .949 |
| 9 | 21,111 | 2.618 | 1.358 | .942 |
| 10 | 23,181 | 2.874 | 1.375 | .936 |
| 11 | 25,223 | 3.128 | 1.393 | .931 |
| 12 | 27,235 | 3.377 | 1.410 | .926 |
| 13 | 29,218 | 3.623 | 1.427 | .921 |
| 14 | 31,171 | 3.865 | 1.447 | .919 |
| 15 | 33,096 | 4.104 | 1.462 | .912 |
| 16 | 34,988 | 4.339 | 1.477 | .907 |
| 17 | 36,859 | 4.571 | 1.496 | .904 |
| 18 | 38,688 | 4.797 | 1.512 | .900 |
| 19 | 40,493 | 5.021 | 1.528 | .896 |

## TABLE I.- POTENTIAL ENERGY OF STATES OF $N_2$ - Continued

### (b) A $^3\Sigma_u^+$ state

| v | V, cm-1 | V, electron volts | $T_e$ + V, electron volts | $r_{max}$, A | $r_{min}$, A |
|---|---|---|---|---|---|
| 0 | 726.7 | 0.0901 | 6.316 | 1.356 | 1.240 |
| 1 | 2,160 | .2678 | 6.493 | 1.405 | 1.203 |
| 2 | 3,565 | .4421 | 6.668 | 1.442 | 1.180 |
| 3 | 4,942 | .6128 | 6.838 | 1.474 | 1.160 |
| 4 | 6,291 | .7801 | 7.006 | 1.503 | 1.145 |
| 5 | 7,613 | .9440 | 7.170 | 1.532 | 1.131 |
| 6 | 8,906 | 1.104 | 7.330 | 1.558 | 1.120 |
| 7 | 10,172 | 1.261 | 7.487 | 1.584 | 1.108 |
| 8 | 11,408 | 1.415 | 7.640 | 1.609 | 1.099 |
| 9 | 12,616 | 1.564 | 7.790 | 1.633 | 1.089 |
| 10 | 13,793 | 1.710 | 7.936 | 1.657 | 1.080 |
| 11 | 14,942 | 1.853 | 8.079 | 1.682 | 1.070 |
| 12 | 16,060 | 1.991 | 8.217 | 1.706 | 1.062 |
| 13 | 17,147 | 2.126 | 8.352 | 1.732 | 1.054 |
| 14 | 18,203 | 2.257 | 8.483 | 1.756 | 1.046 |

## TABLE I.- POTENTIAL ENERGY OF STATES OF $N_2$ - Continued

### (c) B $^3\Pi_g$ state

| v | V, $cm^{-1}$ | V, electron volts | $T_e$ + V, electron volts | $r_{max}$, A | $r_{min}$, A |
|---|---|---|---|---|---|
| 0 | 863.4 | 0.1071 | 7.501 | 1.271 | 1.165 |
| 1 | 2,569 | .3186 | 7.713 | 1.316 | 1.132 |
| 2 | 4,246 | .5265 | 7.921 | 1.351 | 1.111 |
| 3 | 5,894 | .7309 | 8.125 | 1.381 | 1.095 |
| 4 | 7,512 | .9315 | 8.325 | 1.409 | 1.082 |
| 5 | 9,101 | 1.129 | 8.523 | 1.436 | 1.071 |
| 6 | 10,661 | 1.322 | 8.716 | 1.460 | 1.061 |
| 7 | 12,191 | 1.512 | 8.906 | 1.484 | 1.052 |
| 8 | 13,693 | 1.698 | 9.092 | 1.508 | 1.044 |
| 9 | 15,165 | 1.880 | 9.274 | 1.531 | 1.037 |
| 10 | 16,608 | 2.059 | 9.453 | 1.554 | 1.030 |
| 11 | 18,021 | 2.235 | 9.629 | 1.577 | 1.024 |
| 12 | 19,404 | 2.406 | 9.800 | 1.599 | 1.018 |
| 13 | 20,757 | 2.574 | 9.968 | 1.622 | 1.012 |
| 14 | 22,080 | 2.738 | 10.132 | 1.644 | 1.006 |
| 15 | 23,372 | 2.898 | 10.292 | 1.667 | 1.002 |
| 16 | 24,633 | 3.054 | 10.448 | 1.690 | .996 |
| 17 | 25,862 | 3.207 | 10.601 | 1.714 | .992 |
| 18 | 27,059 | 3.355 | 10.749 | 1.737 | .987 |
| 19 | 28,223 | 3.500 | 10.894 | 1.760 | .983 |

## TABLE I.- POTENTIAL ENERGY OF STATES OF $N_2$ - Continued

### (d) a $^1\Pi_g$ state

| v | V, $cm^{-1}$ | V, electron volts | $T_e$ + V, electron volts | $r_{max}$, A | $r_{min}$, A |
|---|---|---|---|---|---|
| 0 | 839.9 | 0.1041 | 8.696 | 1.278 | 1.172 |
| 1 | 2,506 | .3107 | 8.902 | 1.325 | 1.139 |
| 2 | 4,144 | .5139 | 9.105 | 1.360 | 1.118 |
| 3 | 5,755 | .7136 | 9.305 | 1.391 | 1.101 |
| 4 | 7,338 | .9099 | 9.501 | 1.418 | 1.088 |
| 5 | 8,893 | 1.103 | 9.694 | 1.445 | 1.077 |
| 6 | 10,421 | 1.292 | 9.883 | 1.471 | 1.067 |
| 7 | 11,922 | 1.478 | 10.069 | 1.495 | 1.059 |
| 8 | 13,395 | 1.661 | 10.252 | 1.518 | 1.050 |
| 9 | 14,838 | 1.840 | 10.431 | 1.541 | 1.043 |
| 10 | 16,256 | 2.016 | 10.607 | 1.564 | 1.036 |
| 11 | 17,647 | 2.188 | 10.779 | 1.587 | 1.029 |
| 12 | 19,011 | 2.357 | 10.948 | 1.610 | 1.024 |
| 13 | 20,348 | 2.523 | 11.114 | 1.632 | 1.018 |
| 14 | 21,660 | 2.686 | 11.277 | 1.655 | 1.013 |

## TABLE I.- POTENTIAL ENERGY OF STATES OF $N_2$ - Concluded

### (e) C $^3\Pi_u$ state

| v | V, $cm^{-1}$ | V, electron volts | $T_e$ + V, electron volts | $r_{max}$, A | $r_{min}$, A |
|---|---|---|---|---|---|
| 0 | 1,013 | 0.1256 | 11.180 | 1.202 | 1.104 |
| 1 | 3,006 | .3727 | 11.427 | 1.246 | 1.074 |
| 2 | 4,946 | .6133 | 11.668 | 1.279 | 1.056 |
| 3 | 6,820 | .8457 | 11.900 | 1.310 | 1.042 |
| 4 | 8,602 | 1.067 | 12.121 | 1.342 | 1.033 |

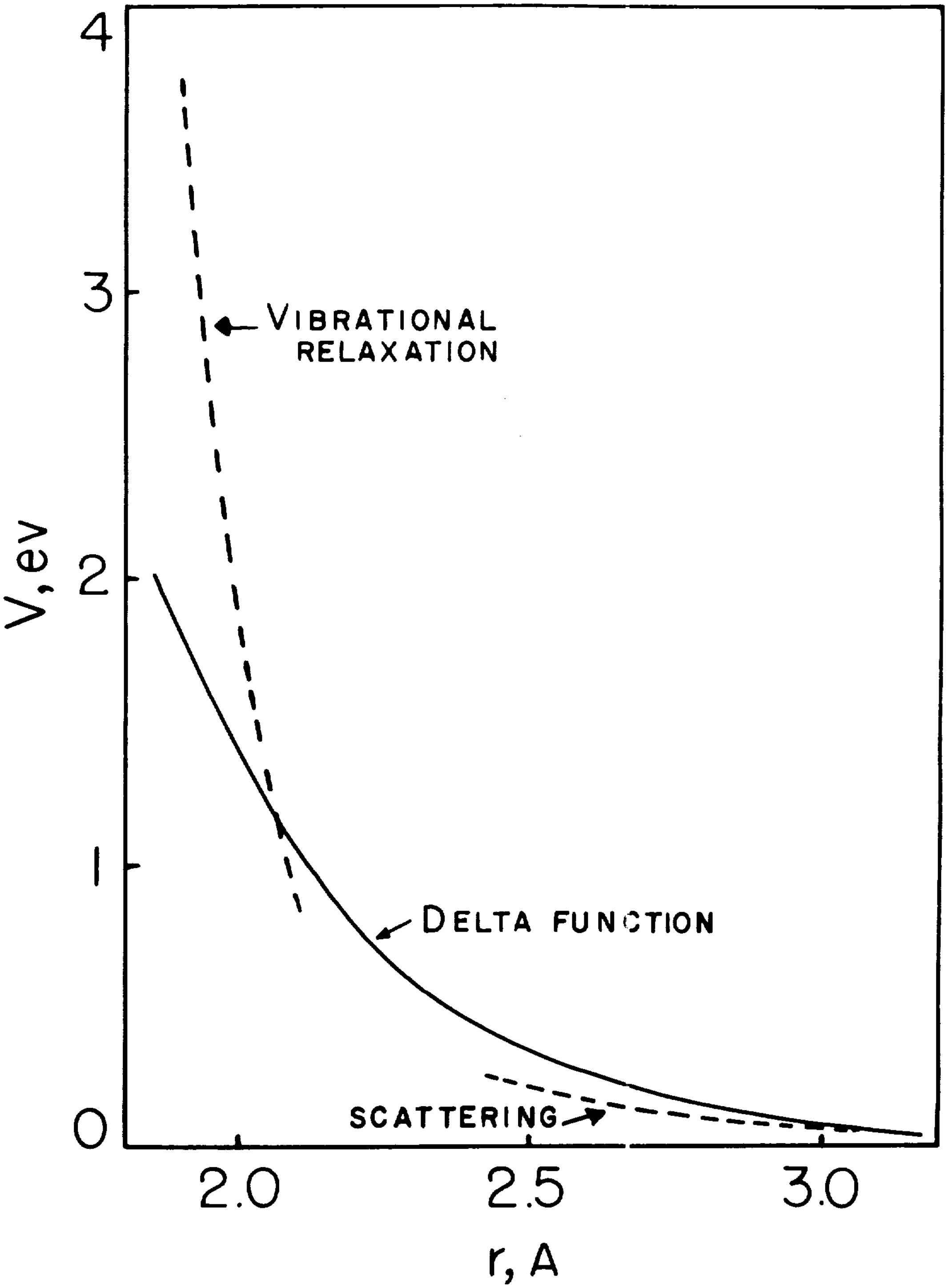


Figure 1.- Energy of $^7\Sigma_u^+$ state of $N_2$ as obtained by different methods.

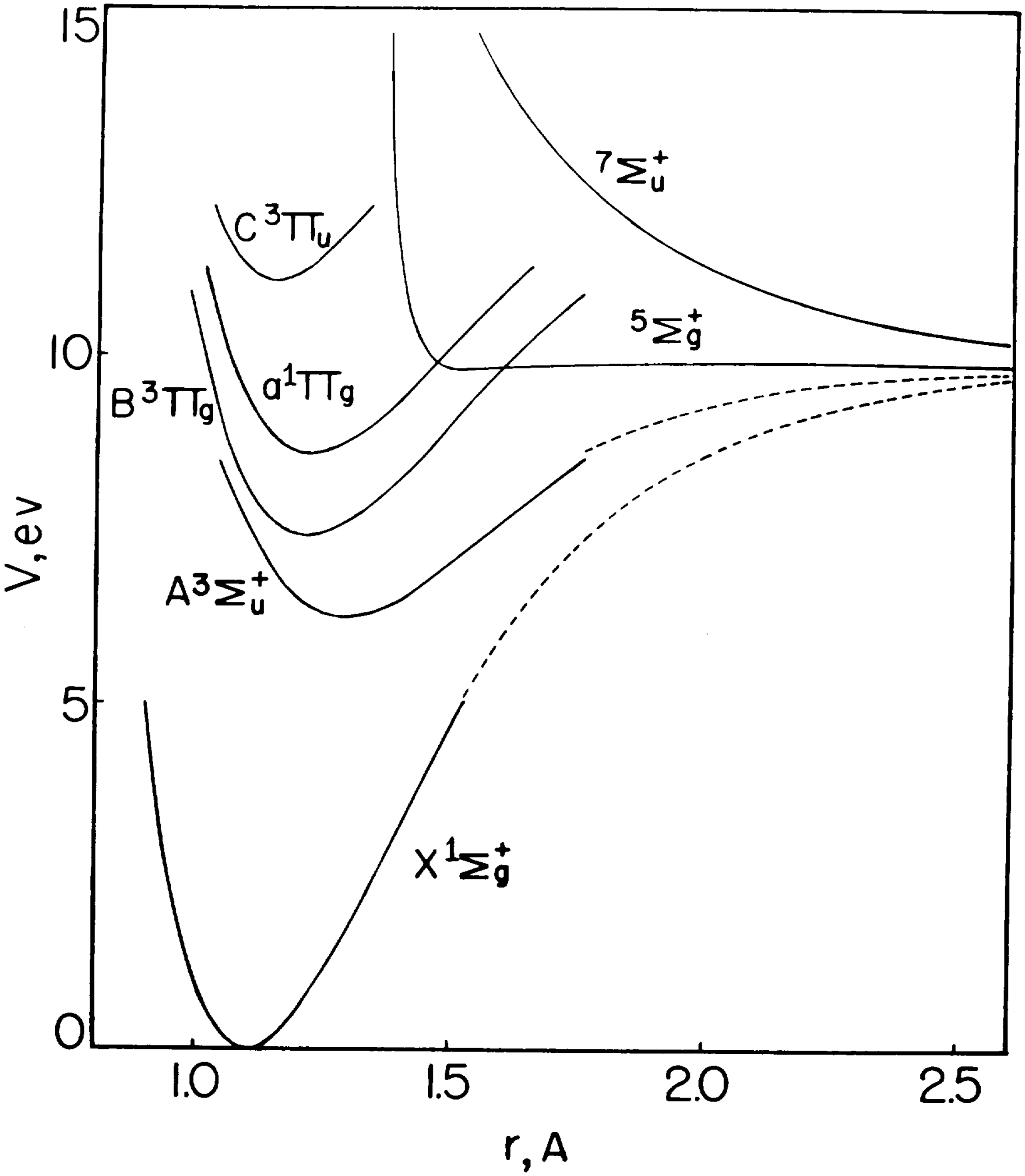
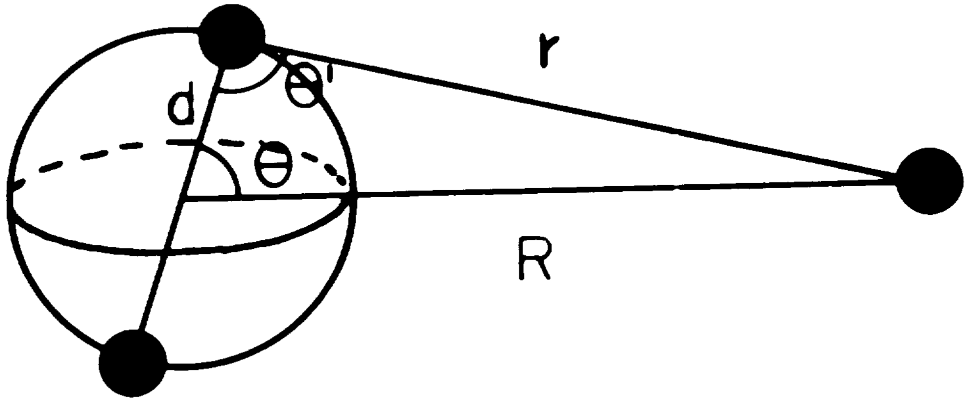
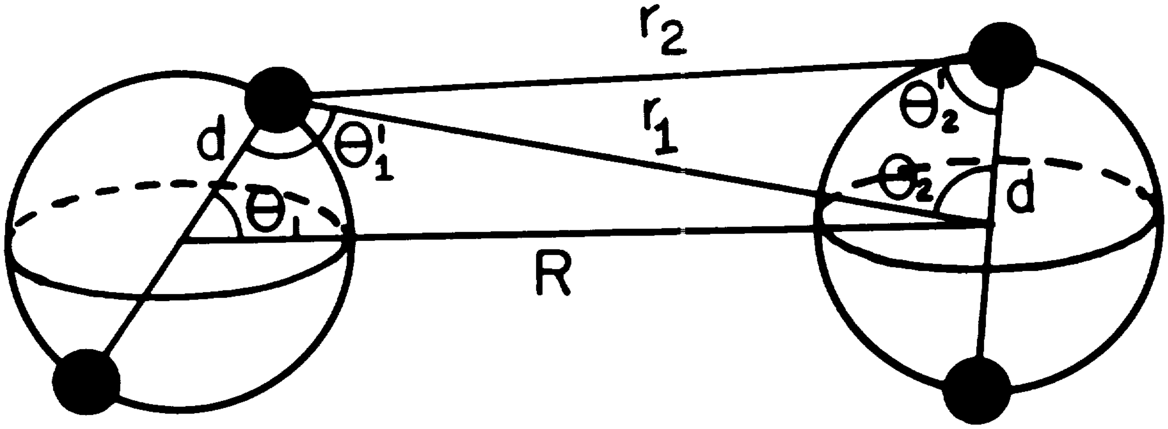


Figure 2.- Summary of N-N interactions.



(a) Atom-molecule interaction.



(b) Molecule-molecule interaction.

Figure 3.- Coordinate systems for averaging interaction energies over molecular orientations.

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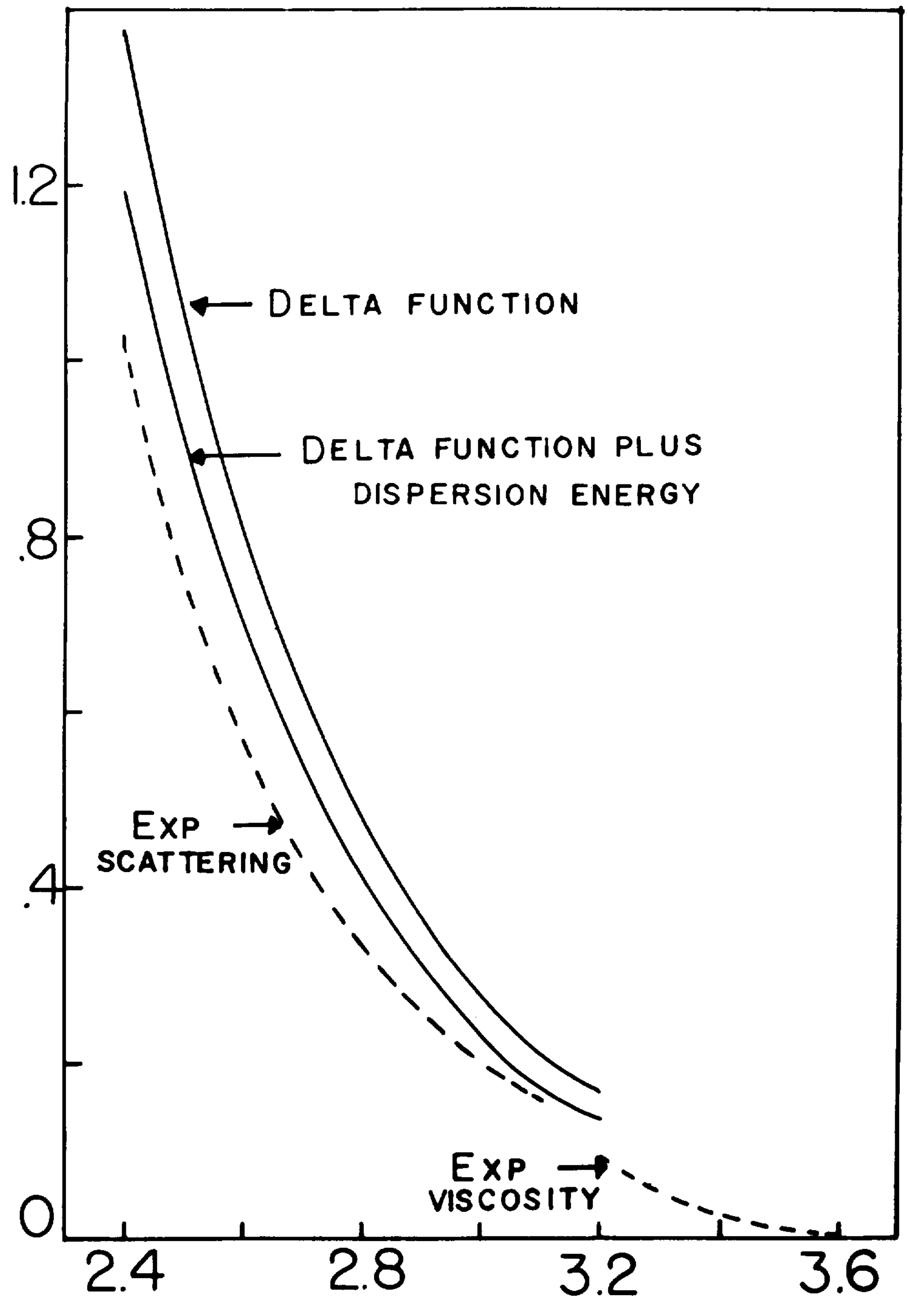

Figure 4.- Average $N_2$-$N_2$ interaction energy as obtained by different methods.