

Electric Dipole Moments of Rare-Gas Diatomic Molecules

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Electric dipole moment and interatomic potential functions are computed for the diatomic systems HeNe, HeAr, and NeAr, in the molecular Hartree-Fock approximation. Since this approximation does not include a description of dispersion forces, the potential curves are purely repulsive. The potential and moment functions can all be fitted closely by simple exponential functions over the range of internuclear distances considered, $2.0 \leq R \leq 5.5a_0$ (Bohr units). The relationship of these functions to recent studies of collision-induced infrared absorption in rare-gas mixtures is discussed. The results can be understood qualitatively in terms of a simple model of atomic moments induced because the exclusion principle causes electrons to be displaced with respect to nuclei during a collision of molecular systems.

I. INTRODUCTION

COLLISION-induced infrared absorption in rare-gas mixtures was originally observed by Kiss and Welsh,¹ and attributed by them to the transient electric dipole moment that exists during the collision of two inequivalent rare-gas atoms. These observations were extended into the far infrared by Bosomworth and Gush,² who observed broad, singly peaked absorption bands for HeAr and NeAr.

The theory of this absorption was considered by Poll and Van Kranendonk,³ who derived an expression for the integrated absorption coefficient in terms of the induced diatomic electric dipole moment. A theory of the absorption band shape has been developed by Tanimoto,⁴ assuming that both the interatomic potential and the induced dipole moment can be approximated by simple exponential functions of the nuclear separation. A classical theory of the band shape has been developed by Levine and Birnbaum,⁵ and is in good agreement with the observed data.

In recent years, it has become possible to compute approximate Hartree-Fock electronic wave functions for diatomic molecules containing atoms in the first third of the periodic table. Computed electric dipole moments, especially for singly bonded molecules, are in very good agreement with experiment.⁶ The purpose of the present work is to carry out similar calculations on the diatomic systems HeNe, HeAr, and NeAr, in order to obtain dipole moment and interatomic potential functions for use in the theory of the induced infrared absorption.

In preliminary calculations,⁷ using computer pro-

grams that are now becoming obsolete,⁸ it was found that the collisions represented by He₂, Ne₂, and HeNe involve very similar changes in the electronic charge distributions. If the Hartree-Fock electronic wave functions of He₂ and of Ne₂ are represented in terms of localized orbitals,⁹ the molecular wave functions describe two colliding atoms. In each atom the electronic cloud is pushed outward with respect to its nucleus, as a consequence of the exclusion principle, as the two electronic clouds are brought into contact. This induces a net atomic moment that decreases approximately as an exponential function of the internuclear separation R . If the two atoms are identical, these induced atomic moments are equal and opposite, and there is no net molecular moment. However, when the atoms differ, a molecular moment appears because the induced atomic moments differ in magnitude. Because the collision radius of an atom is known empirically to be insensitive to the nature of the collision, this implies that the induced atomic moment at the atomic collision radius should be a fairly well-defined property of a rare-gas atom. Preliminary calculations on He₂ indicated an atomic moment of 0.00114 D at the collision diameter, $4.98a_0$. For Ne₂ a moment of 0.00056 D was computed at collision diameter $5.20a_0$. The model suggested above would imply that HeNe should have a net moment, given by the difference of these atomic moments, of 0.00058 D, with polarity He⁻Ne⁺ at internuclear distance $5.09a_0$, the sum of the atomic collision radii. This is in substantial agreement with results computed directly for the system HeNe. The work reported in the present paper gives a moment of 0.00034 D, polarity He⁻Ne⁺, at $5.09a_0$.

While the general phenomenon of collision induced moments can be understood as indicated above, it is desirable to have some reliable data on heteroatomic rare-gas systems over a range of internuclear distances. The approximate Hartree-Fock calculations reported

¹ Z. J. Kiss and H. L. Welsh, *Phys. Rev. Letters* **2**, 166 (1959).

² D. R. Bosomworth and H. P. Gush, *Can. J. Phys.* **43**, 751 (1965).

³ J. D. Poll and J. Van Kranendonk, *Can. J. Phys.* **39**, 189 (1961).

⁴ O. Tanimoto, *Progr. Theoret. Phys. (Kyoto)* **33**, 585 (1965).

⁵ H. B. Levine and G. Birnbaum, *Phys. Rev.* **154**, 86 (1967).

⁶ R. K. Nesbet, *J. Chem. Phys.* **43**, 530 (1965); *Advan. Quantum Chem.* **3**, 1 (1966).

⁷ R. K. Nesbet (unpublished).

⁸ R. K. Nesbet, *Rev. Mod. Phys.* **32**, 272 (1960).

⁹ J. E. Lennard-Jones, *Proc. Roy. Soc. (London)* **A198**, 1 (1949); **A198**, 14 (1949).

here represent the molecular orbital functions as linear combinations of atomic basis orbitals, selected to give a good approximation to the atomic Hartree-Fock orbitals and to allow the molecular orbitals to be polarized or distorted by the molecular environment. This is accomplished by adding to orbital basis sets used for Hartree-Fock calculations on He,¹⁰ Ne,¹¹ and Ar¹² a number of functions with higher angular quantum numbers, to allow for orbital polarization. Preliminary calculations, needed to explore various choices of basis orbitals, are described in Sec. II. The principal results of this paper, the dipole moment and the interatomic potential functions, are described in Sec. III.

The calculations reported here were carried out with

TABLE I. Basis orbital parameters for HeNe.

Atom	Type	Exponent	Atom	Type	Exponent
He	1s	1.450	Ne	1s	15.439
	2s σ	2.641		1s σ	8.806
	2s σ	1.723		2s σ	3.764
	2p σ	1.4197		2s σ	2.301
	2p π	2.2479		3s σ	10.995
				2p σ	10.542
				2p σ	4.956
				2p σ	2.793
				2p σ	1.623
				3d σ	2.0438
		2p π	10.542		
		2p π	4.956		
		2p π	2.793		
		2p π	1.623		
		3d π	2.3414		

efficient and accurate computer programs recently developed by McLean and Yoshimine.¹³

II. PRELIMINARY COMPUTATIONS

Exploratory calculations on HeNe designed to determine the influence of various possible polarization functions on the dipole moment were performed at $R=2.0$ using double zeta¹⁴ atomic Hartree-Fock basis sets augmented by various combinations of $2p_{\sigma,\pi}$, $3d_{\sigma,\pi}$, and $4f_{\sigma,\pi}$ atomic orbitals on He and $3d_{\sigma,\pi}$ and $4f_{\sigma,\pi}$ atomic

¹⁰ P. S. Bagus (unpublished).

¹¹ P. S. Bagus, Phys. Rev. **139**, A619 (1965).

¹² E. Clementi, IBM J. Res. Develop. **9**, Suppl. (1965), Table 31-01.

¹³ A. D. McLean and M. Yoshimine, Program 104, Quantum Chemistry Program Exchange, Indiana University 1966, (unpublished).

¹⁴ E. Clementi, J. Chem. Phys. **40**, 1944 (1964).

TABLE II. Basis orbital parameters for HeAr.

Atom	Type	Exponent	Atom	Type	Exponent
He	1s σ	1.450	Ar	1s σ	18.0291
	2s σ	2.641		1s σ	29.720
	2s σ	1.723		2s σ	6.7597
	2p σ	1.2772		2s σ	16.000
	2p π	2.095		3s σ	3.6625
				3s σ	2.0877
		3s σ		4.800	
		2p σ		8.1006	
		2p σ		14.4788	
		3p σ		2.9031	
		3p σ		1.6098	
		3p σ		6.4009	
		3d σ		2.4709	
		2p π		8.1006	
		2p π		14.4788	
		3p π		2.9031	
		3p π	1.6098		
		3p π	6.4009		
		3d π	2.0613		

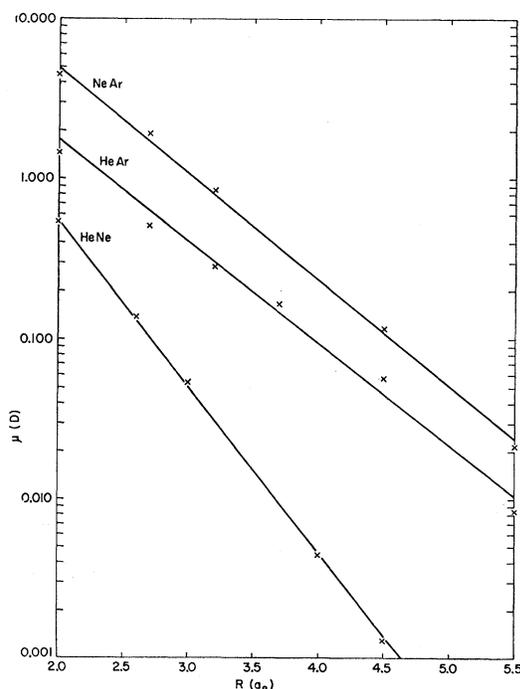


FIG. 1. Computed electric dipole moments μ in Debye units (D) plotted against nuclear separation R in Bohr atomic units (a_0). Computed points are indicated. The heavy lines are simple exponential functions fitted to these points, $\mu = A_\mu \exp(-\lambda_\mu R)$. The parameters for the moments He⁻Ne⁺, He⁺Ar⁻, Ne⁺Ar⁻ are, respectively, $A_\mu = 66.948, 33.707, 105.15$ and $\lambda_\mu = 2.397, 1.472, 1.528$.

TABLE III. Basis orbital parameters for NeAr.

Atom	Type	Exponent	Atom	Type	Exponent
Ne	1s σ	15.439	Ar	1s σ	18.0291
	1s σ	8.806		1s σ	29.720
	2s σ	3.764		2s σ	6.7597
	2s σ	2.301		2s σ	16.000
	3s σ	10.995		3s σ	3.6625
	2p σ	10.542		3s σ	2.0877
	2p σ	4.956		3s σ	4.800
	2p σ	2.793		2p σ	8.1006
	2p σ	1.623		2p σ	14.4788
	3d σ	2.0438		3p σ	2.9031
	2p π	10.542		3p σ	1.6098
	2p π	4.956		3p σ	6.4009
	2p π	2.793		3d σ	2.4709
	2p π	1.623		2p π	8.1006
	3d π	2.3414		2p π	14.4788
				3p π	2.9031
				3p π	1.6098
		3p π	6.4009		
		3d π	2.0613		

orbitals on Ne. The only functions which were found to make a significant contribution to μ were the $2p_{\sigma,\pi}$ orbitals on He and the $3d_{\sigma,\pi}$ orbitals on Ne.

It was assumed that a similar situation existed for Ar. Thus, in preliminary calculations on this molecule, also performed at $R=2.0$, it was necessary only to determine optimal exponent values for the $3d_{\sigma,\pi}$ functions on Ar and to ascertain whether or not the optimized values of the $2p_{\sigma,\pi}$ functions on He were transferable to HeAr. It was found that reoptimization of these functions had no significant effect on either the total energy or the dipole moment.

Since the $2p_{\sigma,\pi}$ functions on He were transferable, it was assumed that the same would be true of the $3d_{\sigma,\pi}$ functions on Ne and Ar. Thus, no preliminary calculations

TABLE IV. Computed interatomic potential V and electric dipole moment μ of HeNe at various internuclear distances R . V is relative to the computed Hartree-Fock energy of the separated atoms, -131.40878 Hartree atomic units (e^2/a_0). The polarity of μ is He $^-$ Ne $^+$.

R (a_0)	V (e^2/a_0)	μ (D)
2.0	0.3183	0.5374
2.6	0.0828	0.1371
3.0	0.0332	0.0540
4.0	0.0032	0.0045
4.5	0.0010	0.0013
5.0	0.0003	0.0005

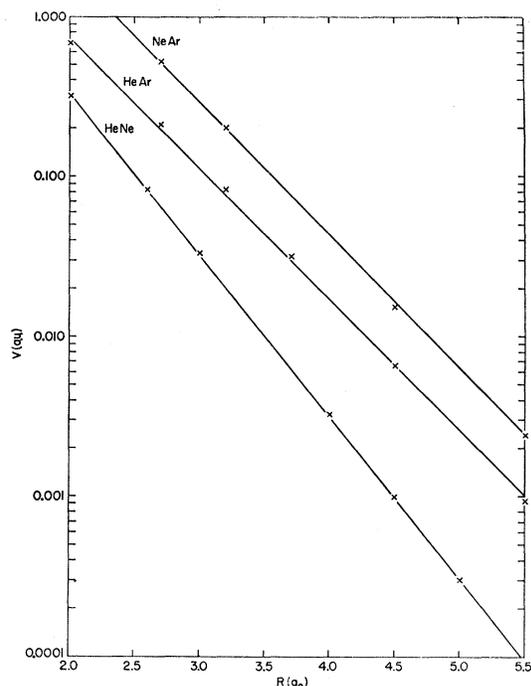


FIG. 2. Computed interatomic potential energy V in Hartree atomic units (e^2/a_0), relative to Hartree-Fock energy of separated atoms, plotted against nuclear separation R in Bohr atomic units (a_0). Computed points are indicated. The heavy lines are simple exponential functions fitted to these points, $V = A_v \exp(-\lambda_v R)$. The parameters for HeNe, HeAr, NeAr are, respectively, $A_v = 33.418, 31.395, 92.544$ and $\lambda_v = 2.322, 1.884, 1.923$.

were performed on NeAr. Orbital exponent values were taken directly from the HeNe and HeAr calculations.

The orbital basis sets used for the final results reported in the last section are indicated in Tables I-III.

III. FINAL RESULTS

The computed interatomic potentials and dipole moments are given for HeNe, HeAr, and NeAr in Tables

TABLE V. Computed interatomic potential V and electric dipole moment μ of HeAr at various internuclear distances R . V is relative to the computed Hartree-Fock energy of the separated atoms, -529.67873 Hartree atomic units. The polarity of μ is He $^+$ Ar $^-$.

R (a_0)	V (e^2/a_0)	μ (D)
2.0	0.6806	1.4520
2.7	0.2082	0.5064
3.2	0.0820	0.2850
3.7	0.0315	0.1659
4.5	0.0065	0.0577
5.5	0.0009	0.0084

IV–VI, respectively. The computed points are indicated in Figs. 1 and 2. Also included in the figures are plots of simple exponential functions with parameters chosen to fit the computed points. It can be seen from these figures that the simple exponential form used by Tanimoto⁴ is a good qualitative representation of these results, both for the dipole moment and potential function. It should be pointed out that the Hartree-Fock approximation used here cannot describe the correlation effect responsible for the dispersion force or van der Waals interaction. Hence, the purely repulsive potential functions derived here must be modified by inclusion of the van der Waals potential, asymptotically proportional to R^{-6} .

At large values of R , the numerical cancellation involved in calculating both μ and V is severe. For this reason the present results become less reliable as R increases. The calculations were carried out at values of R smaller than the atomic collision diameters to provide a more reliable extrapolation into the physically meaningful region.

IV. DISCUSSION

Since Figs. 1 and 2 indicate that the computed results are well represented by simple exponential functions, the quantitative results can be summarized by the parameters A and λ that determine each of these curves, given in the figure captions. The good agreement with experimental band shapes obtained by Levine and Birnbaum,⁵ who assumed a Gaussian form for $\mu(R)$, indicates that the absorption band shape is insensitive to the functional form of the dipole moment function. In this situation, the parameters A and λ contain about as much information as can usefully be compared with experiment.

Figure 1 indicates that $\mu(R)$ for both NeAr and HeAr is more than an order of magnitude greater than $\mu(R)$ for HeNe for values of R comparable to collision diameters, and the exponential decrease of the latter function is much faster. This is in agreement with the experimental observation that the HeNe absorption is considerably weaker than the other two.

The dipole moment functions shown in Fig. 1 have a simple interpretation in terms of the induced atomic moments discussed in the Introduction. The moment

TABLE VI. Computed interatomic potential V and electric dipole moment μ of NeAr at various internuclear distances R . V is relative to the computed Hartree-Fock energy of the separated atoms, -655.36415 Hartree atomic units. The polarity of μ is Ne^+Ar^- .

R (a_0)	V (e^2/a_0)	μ (D)
2.0	1.6270	4.4780
2.7	0.5204	1.9111
3.2	0.1989	0.8494
4.5	0.0151	0.1163
5.5	0.0024	0.0213

of HeNe has polarity He^-Ne^+ , indicating that the atomic moment of He is greater than that of Ne throughout the range of R considered here. If it is assumed that the atomic moment of Ar is larger than either that of He or Ne, it follows for the magnitudes of the net diatomic moments that $\mu(\text{HeAr}) < \mu(\text{NeAr})$, and the polarities must be He^+Ar^- and Ne^+Ar^- , in agreement with the computed results. Furthermore, the $\mu(R)$ functions for HeAr and NeAr should be dominated by the dependence on R of the Ar atomic moment, while the HeNe moment function should be dominated by the He atomic moment. This is consistent with the near equality of the exponents λ of the HeAr and NeAr functions in Fig. 1 both significantly different from the exponent of the HeNe function.

A similar process must occur when any two molecular systems collide—the exclusion principle displaces the electronic cloud backward with respect to the nuclear framework, and an induced transient dipole moment occurs if the colliding systems are not identical. Since radiation will be emitted in any such process, this provides a simple universal mechanism for the thermal degradation of kinetic energy, effective independently of the existence of permanent electric moments.

ACKNOWLEDGMENT

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