Molecular beam studies of openshell systems: The van der Waals interaction between O(3 P) and He(1 S)

V. Aquilanti, R. Candori, E. Luzzatti, F. Pirani, and G. G. Volpi

Citation: The Journal of Chemical Physics **85**, 5377 (1986); doi: 10.1063/1.451159
View online: http://dx.doi.org/10.1063/1.451159
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/85/9?ver=pdfcov
Published by the AIP Publishing

[3]G. L. Millhauser and J. H. Freed, J. Chem. Phys. 81, 37 (1984).
[4]L. J. Schwartz, G. L. Millhauser, and J. H. Freed, Chem. Phys. Lett. 127, 60 (1986).
[5]J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, J. Chem. Phys. 71, 11 (1979).
[6]A. E. Stillman and R. N. Schwartz, J. Phys. Chem. 85, 3031 (1981).
[7]H. Borsboom (private communication).
[8]R. P. J. Merks and R. deBeer, J. Phys. Chem. 83, 3319 (1979).
[9]J. H. Freed, J. Chem. Phys. 45, 3452 (1966).
[10]M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, J. Chem. Phys. 51, 2690 (1969).
[11]R. N. Schwartz, L. L. Jones, and M. K. Bowman, J. Phys. Chem. 83, 3429 (1979).
[12]L. J. Schwartz, Ph.D. thesis Cornell University, 1984; L. J. Schwartz and J. H. Freed (to be published).
[13]J. Keeler and D. Neuhaus, J. Magn. Reson. 63, 454 (1985).
[14]W. P. Aue, E. Bartholdi, and R. R. Ernst, J. Chem. Phys. 64, 2229 (1976).
[15]D. J. States, R. A. Haberkorn, and D. J. Ruben, J. Magn. Reson. 48, 286 (1982).
[16]P. Bachmann, W. P. Aue, L. Muller, and R. R. Ernst, J. Magn. Reson. 28, 29 (1977).
[17]J. S. Hyde, J. C. W. Chien, and Jack H. Freed, J. Chem. Phys. 48, 4211 (1968).
[18]J. H. Freed, in *Time Domain Electron Spin Resonance*, edited by L. N. Kevan and R. N. Schwartz (Wiley, New York, 1979), Chap. 2.
[19]J. P. Hornak and J. H. Freed, Chem. Phys. Lett. 101, 115 (1983).
[20]J. S. Hwang, R. P. Mason, L. P. Hwang, and J. H. Freed, J. Phys. Chem. 79, 489 (1975).
[21]A. Bax, *Two-Dimensional Nuclear Magnetic Resonance in Liquids* (Reidel, Boston, 1984), pp. 95, 181, 61.

NOTES

Molecular beam studies of open-shell systems: The van der Waals interaction between O(^3P) and He(^1S)

V. Aquilanti, R. Candori, E. Luzzatti,[a] F. Pirani, and G. G. Volpi
Dipartimento di Chimica dell'Università, 06100 Perugia, Italy

(Received 2 June 1986; accepted 14 July 1986)

A first attempt to obtain information on the interaction between helium and ground state oxygen atoms was reported many years ago from this laboratory[1]: Only an estimate of the average potential could be given. Recently, an extensive computational study[2] has been devoted to this system, which is basic to our understanding of the nature of the interactions of open shell atoms. In this Note, new experimental results on this system are reported, and the available information is shown to provide an assessment of the main features of the involved interaction.

The results, which supersede the old ones, are shown in Fig. 1: The absolute integral cross sections have been obtained as a function of velocity employing the apparatus described previously[3] and used recently for the study of the interaction of F(^2P) atoms with rare gases,[4] of O(^3P) with Ar, Kr, and Xe,[3] of N atoms with Ar[5] and Kr.[6] The oxygen atom beam is velocity selected to better than 5%, and a Stern–Gerlach magnet (Rabi configuration) provides a control of the atomic magnetic sublevels.

These low energy integral cross section experiments can be interpreted by assuming that the collision takes place adiabatically along six effective potential energy curves, labeled by the quantum numbers of atomic angular momentun $j = 2,1,0$ and its projection $\Omega = |m_j|$. These curves are related to the electrostatic potentials v_Σ and v_Π by the formulas given in the Appendix of Ref. 3.

A variation of the magnetic field intensity allows a variation of the relative population of the $|j\Omega\rangle$ states: The results in Fig. 1 show that the difference of cross sections for two extreme cases is minor, indicating that the anisotropy of the involved interaction is small.

A calculation of the integral elastic cross sections for the present experimental conditions using the v_Σ and v_Π interactions obtained by the CEPA technique of Staemmler and Jaquet[2] is shown (dotted curves in Fig. 1) to reproduce the overall behavior but to underestimate the absolute magnitude. An extrapolation procedure on their computed potentials lead Staemmler and Jaquet,[2] to propose improved v_Σ and v_Π interactions which actually, as shown in Fig. 1 (dashed curves), yield integral cross sections much closer to our measurements. We take this as evidence that, although the computed values underestimate the cross sections, the extrapolation procedure indicates correctly in which direction a substantial improvement can be achieved.

Our procedure thus starts by assuming that the *anisotropy*[7] $v_2 = \frac{5}{3}(v_\Sigma - v_\Pi)$ is correctly given by CEPA calculation. In fact, it can be verified, at least for the range of distances probed by our experiment (i.e., where van der Waals minima occur) that the extrapolation procedure proposed by Staemmler and Jaquet does not modify substantially the *difference* $v_\Sigma - v_\Pi$. Actually, some evidence is being accumulated for other systems in our laboratory[8] that, because of error cancellations, such a difference can be estimated even from not too sophisticated calculations better than the individual contributions. Having fixed the anisotropy v_2, we then adjusted the *spherical*[7] interaction $v_0 = \frac{1}{3}(v_\Sigma + 2v_\Pi)$ by using a sufficiently flexible form to fit our data. The results of such a procedure are shown in Fig. 1 (continuous curve),

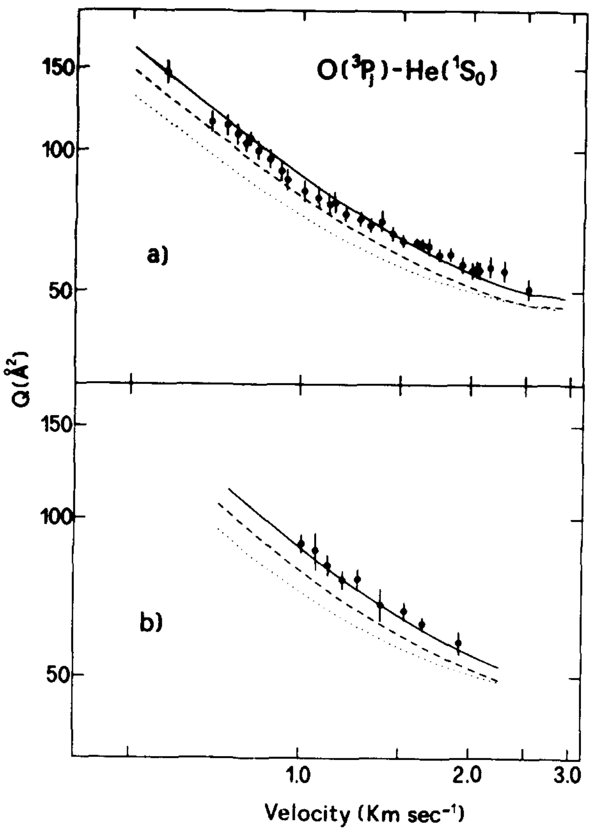

FIG. 1. Absolute integral elastic cross sections Q for collisions between $O(^3P_j)$ and $He(^1S)$ atoms as a function of velocity. In (a), the measurements are taken at zero field in the magnetic analyzer, corresponding [see Refs. 3 and 7(a)] to essentially statistical distribution of $|j\Omega\rangle$ states; in (b), the applied field B ($B/v^2 = 0.15$ T Km^{-2} s^{-2}, where v is the measured velocity of oxygen atoms) deflects completely the $|2,1\rangle$ and $|1,0\rangle$ states, and corresponds to the distributions given in Ref. 3). The dotted and broken curves are calculated with the CEPA and extrapolated interactions computed in Ref. 2. The continuous curves correspond to the interactions proposed in this work.

and lead to the characterization of the involved spherical interaction as having a well depth of 2.1 meV at a distance of 3.27 Å.[9] The electrostatic potentials are assessed to have a well depth of 1.4 meV for v_Σ and 3.0 meV for v_Π, at distances 3.54 and 3.06 Å, respectively.[9] The ground adiabatic state is found to be purely π in character, similarly to what is found[3] for the heavier rare gases: in case (c) designation Ω_j is 2_2, and $^3\Pi_2$ in case (b) designation.

Other features of this interaction, and more details about the experiments and their analysis, will be presented in a future publication, together with a reexamination of the interaction of $O(^3P)$ atoms with all the other rare gases. A conclusion from this work is that even moderately sophisticated quantum mechanical computations for diatomic systems containing a few electrons (ten in this case), such as the CEPA results of Ref. 2, appear to underestimate the van der Waals well depths by as much as 30%–40%.

This research is supported by the Ministero della Pubblica Istruzione and by the Italian National Research Council (CNR), also through a Bilateral Project with the Deutsche Forschungsgemeinschaft.

[a] On leave from Istituto di Metodologie Avanzate Inorganiche del Consiglio Nazionale delle Ricerche, Area della Ricerca di Roma-00016 Monterotondo Scalo-Italy.

[1] V. Aquilanti, G. Liuti, F. Pirani, F. Vecchiocattivi, and G. G. Volpi, J. Chem. Phys. **65**, 4751 (1976).
[2] V. Staemmler and R. Jaquet, Chem. Phys. **92**, 141 (1985) report an extensive quantum chemical calculation including the electronic correlation by the correlated electron pair approximation (CEPA).
[3] V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, J. Chem. Phys. **73**, 1181 (1980).
[4] V. Aquilanti, E. Luzzatti, F. Pirani, and G. G. Volpi, Chem. Phys. Lett. **90**, 382 (1982); in *Electronic and Atomic Collisions*, Abstracts of XIV ICPEAC, edited by M. J. Coggiola, D. L. Heustis, and R. P. Saxton (Palo Alto, CA, 1985), p. 350.
[5] B. Brunetti, G. Liuti, E. Luzzatti, F. Pirani, and G. G. Volpi, J. Chem. Phys. **79**, 273 (1983).
[6] G. Liuti, E. Luzzatti, F. Pirani, and G. G. Volpi, Chem. Phys. Lett. **121**, 559 (1985).
[7] (a) V. Aquilanti, G. Grossi, and F. Pirani, in *Electronic and Atomic Collisions*, invited papers at XIII ICPEAC, edited by J. Eichler, I. V. Hertel, and N. Stolterfoht (North-Holland, Amsterdam, 1983), p. 441; (b) V. Aquilanti and G. Grossi, J. Chem. Phys. **73**, 1165 (1980).
[8] See, for example, the work by B. Brunetti, F. Vecchiocattivi, A. Aguilar-Navarro, and A. Solé, Chem. Phys. Lett. **126**, 245 (1986) on $HeAr^+$ and $NeAr^+$ ions.
[9] Estimated uncertainties are 0.1 meV for well depths and 0.06 Å for distances.