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ION MOBILITIES IN HELIUM†

E. C. Beaty,* J. C. Browne, and A. Dalgarno

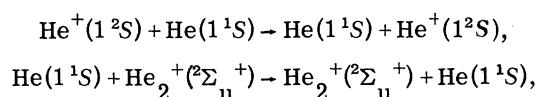
School of Physics and Applied Mathematics, The Queen's University of Belfast, Belfast, Northern Ireland
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Madson, Oskam, and Chanin¹ have recently reported a combined mass analysis and mobility measurement of ions in helium. They reported an ion of mass 4 with a mobility of $10 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ and two ions of mass 8 with mobilities of 16 and $20 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. The mass measurement confirms the identification made in previous,² more precise measurements of the mobility of He^+ and it confirms previous conclusions that the mobility of He_2^+ in the ground state (${}^2\Sigma_u^+$) is about $16.5 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. Madson, Oskam, and Chanin do not attempt to identify the other mass-8 ion beyond noting that it was formed only by a high-voltage spark and that the spark conditions were similar to those used by Biondi and Chanin³ and by Beaty and Patterson,⁴ who also found ions with mobilities of about $20 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

We suggest that the fastest ion is the metastable ${}^4\Sigma_u^+$ state of He_2^+ .

A configuration-interaction valence-bond calculation of the potential curve of the state, which arises from the interaction of $\text{He}^+(1^2S)$ and $\text{He}(2^3S)$, shows that it has a binding energy of at least 1.1 eV, 1.1 eV being the difference between the computed total energy minimum and the experimental energy of the separated atoms. Similar calculations show that the other quartet states of He_2^+ lie above the ${}^4\Sigma_u^+$ state so that the ${}^4\Sigma_u^+$ state is metastable with respect to radiative decay. Figure 1 is a graph of the potential curves of the ${}^4\Sigma_u^+$ and ${}^4\Sigma_g^+$ states.

The proposed identification of the fastest ion provides a plausible explanation of the experimental observations. The spark discharges contain large concentrations of excited triplet He atoms as well as excited ions, permitting the quartet molecules to be formed by two-body processes. Outside the discharge, destruction of the state by collisions is probably very slow. The mobility of $\text{He}_2^+({}^4\Sigma_u^+)$ should be higher than the other ions because it is not affected by resonance processes analogous to



which can be postulated to account for the small mobilities of $\text{He}^+(1^1S)$ and $\text{He}_2^+({}^2\Sigma_u^+)$.

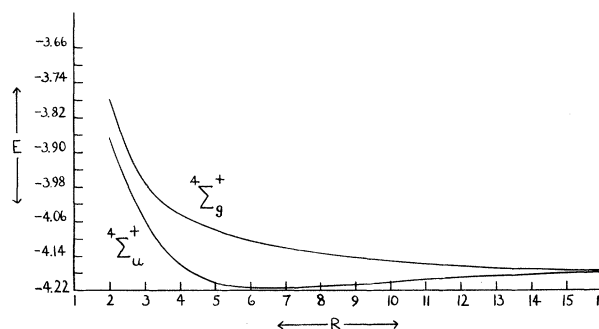


FIG. 1. Potential curves for ${}^4\Sigma_u^+$ and ${}^4\Sigma_g^+$ states of He_2^+ . Energy (E) is in a.u. and internuclear separation (R) is in a_0 .

Vibrational excitation probably does not alter the mobility significantly. Furthermore, the large number of vibrational states would cause an essentially continuous distribution of mobilities which is not consistent with the observations.

He⁺⁺ ions may be produced by the spark discharge and removed only slowly by low-energy collisions with helium atoms. According to unpublished calculations by A. S. Dickinson, the mobility of He⁺⁺ at 300°K is 20.5 cm² V⁻¹ sec⁻¹. But He⁺⁺ would not show up in the mass analysis at mass 8 unless a very efficient conversion process to He₂⁺ were occurring in the entrance slit of the mass spectrometer.

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also go to A. S. Dickinson for allowing us to quote his unpublished results on the mobility of He⁺⁺ in He.

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*Permanent address: Joint Institute for Laboratory Astrophysics, Boulder, Colorado.

¹J. M. Madson, H. J. Oskam, and L. M. Chanin, Phys. Rev. Letters **15**, 1018 (1965).

²See Ref. 1 and E. C. Beaty and P. L. Patterson, Phys. Rev. **137**, A346 (1965), for reviews of the previous work.

³M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

⁴Beaty and Patterson, Ref. 2.

COLLECTIVE OSCILLATIONS OF ATOMS IN THE HARTREE-FOCK APPROXIMATION*

Sol Wieder

Physics Department, New York University, Bronx, New York

and

Sidney Borowitz†‡

Weizmann Institute of Science, Rehovoth, Israel

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There has recently been some interest in the existence of possible collective oscillations in atoms. The atomic cloud is distinguished from the infinite electron plasma by virtue of its inhomogeneity. Collective oscillations for a slightly inhomogeneous electron gas have been analyzed by Sziklas.¹ A schematic as well as a statistical model leading to collective excited states of an atom have been analyzed by Brandt and Lundquist.^{2,3}

The object of this note is to report an estimate of the collective frequency of argon in the Hartree-Fock scheme. Our analysis resembles that of Goldstone and Gottfried⁴ and Nozières and Pines⁵ for infinite electron plasmas. We consider the response of an atom to a long-wavelength radiation field. First-order time-dependent perturbation theory is used to construct a time-dependent Hartree-Fock state from a stationary one.

The unperturbed Hartree-Fock Hamiltonian

is chosen as

$$H_0 = \sum_{i=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{|\vec{r}_i|} + U_{\text{eff}}(\vec{r}_i) \right], \quad (1)$$

while the total Hamiltonian is

$$H(t) = \sum_{i=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{|\vec{r}_i|} + U_{\text{eff}}(\vec{r}_i, t) + U_{\text{app}}(\vec{r}_i, t) \right], \quad (2)$$

with

$$U_{\text{app}}(\vec{r}, t) = eE_0(\omega)ze^{-i\omega t}, \quad (3)$$

and

$$U_{\text{eff}}(\vec{r}, t) = U_{\text{eff}}(\vec{r}) + \delta U_{\text{eff}}(\vec{r}, t). \quad (4)$$