11-18-1993

Response to "Comment on 'The Weakest Bond: Experimental Observation of Helium Dimer'"

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Response to "Comment on 'The weakest bond: Experimental observation of helium dimer' " [J. Chem. Phys. 100, 4021 (1994)]

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(Received 5 August 1993; accepted 18 November 1993)

The arguments made by Meyer, Mester, and Silvera (MMS) in Ref. 1 are based on the helium cluster mass spectral data reported previously by van Deursen and Reuss (vDR),[2] and by Stephens and King (SK),[3] and referred to in our original paper.[4] These authors found no evidence for the presence of He_2 in their experiments, but saw He_2^+ ions created in the electron-bombardment ion sources as fragments of larger clusters $He_n (n \geqslant 3)$.

As a starting point, it is helpful to note the important differences between our experiments and the previous ones. Both the vDR and SK experiments were carried out with continuous beams produced from cryogenic nozzles (T_0 =4.2 to 7 K) having diameters d of a few microns, operated at pressures P_0 of about 1 bar or less, and expanding into small chambers with relatively high background pressures. By using a fast pulsed nozzle with much higher values of P_0 and d, we have been able to achieve submillikelvin translational temperatures for the first time.[5] In addition, operating the pulsed nozzle at T_0=300 K mitigates very strongly against cluster formation. Thus, vDR and SK observed He_2^+/He^+ signal ratios (I_8/I_4) in their mass spectrometers up to about 0.1, while the maximum value of I_8/I_4 seen in our experiments was 2×10^{-4}.

As stated in our original paper, we base our conclusion that we have detected the neutral helium dimer primarily on the pressure dependences of I_8 and I_4. We observed $I_8/I_4 \propto P_0^{1.1\pm0.1}$ over the range of source pressures where the beam temperature is essentially constant. This dependence is in good agreement with that observed by Buck[6] for the dimer to monomer ratio in a pure Ar beam ($Ar_2/Ar \propto P_0^{1.3\pm0.2}$), in experiments where a scattering method was used to eliminate any uncertainty as to the origin of the Ar^+ and Ar_2^+ signals. Our results are very different from those of vDR and SK, who observed $I_8/I_4 \propto P_0^{\sim 2.3}$ at pressures low enough that signals from $He_n^+ (n \geqslant 3)$ are negligible.

The alternative interpretation offered by MMS requires that the I_8 signal in our experiments be due to trimers, and that the trimer population be depleted at the highest pressures by the formation of even larger clusters, thus reducing the dependence of I_8 on P_0. The onset of this "saturation" behavior was seen by vDR and SK at a value of I_8/I_4 equal to about 0.05. What MMS fail to note is that I_8/I_4 in our experiments is *3 orders of magnitude smaller* than that at which vDR and SK observed anything other than an approximately cubic dependence of I_8 on P_0. Also, under conditions where vDR and SK observed "saturation" of I_8, they also observed large signals from He_3^+ and higher cluster ions, as expected under conditions where larger clusters are being formed at the expense of trimer population. I_{12}/I_4 in this regime was about 10^{-2} in the vDR and SK experiments, whereas I_{12} was undetectable in our experiments, with an upper limit of 2×10^{-6} for I_{12}/I_4. Both of these features of our data eliminate the possibility that the nearly quadratic dependence of I_8 and linear dependence of I_8/I_4 on P_0 which we observed could be attributed to depletion of trimer population by the formation of larger clusters. Thus, the alternative hypothesis of MMS is untenable, and neutral He_2 remains the only viable precursor for the He_2^+ signals seen in our experiments.

Although the essential elements of our response to MMS are given above, it seems appropriate that we take this opportunity to clarify some other matters raised in their Comment as well.

(i) The claim made by MMS that larger clusters are preferentially "evaporated" from the beam compared to monomers and smaller clusters is contradicted by both experimental and theoretical results for cluster beams. In fact, to the extent that such separation occurs, momentum effects tend to concentrate larger clusters near the beam centerline.[7]

(ii) The alternative fit to our data of the *ad hoc* form suggested by MMS is indistinguishable in the constant-temperature, high-pressure regime from the limiting behavior reported in our original paper, $I_8 \propto P_0^{1.88\pm0.10}$. The observed falloff of the dimer signal at lower pressures and higher beam temperatures is consistent with the quasiequilibrium model outlined in our original paper and our current best estimate of the He_2 binding energy of 1.2 mK.[8] We have now carried out additional measurements at a source pressure of 125 bar, obtaining translational temperatures of 0.5 ± 0.1 mK for He and 1.1 ± 0.2 mK for He_2. This indicates that the dimers are very nearly equilibrated at the monomer temperature, consistent with the very large scattering lengths which have been estimated theoretically for both species.[9]

(iii) SK did not measure an upper bound of 1.0×10^{-3} on the branching ratio ($He_3 \rightarrow He_3^+/He_3 \rightarrow He_2^+$) as stated by MMS. Instead, they observed $He_3^+/He_2^+ = 10^{-3}$ at their detection limit for He_3^+, and commented that this would be an upper limit to the branching ratio if their He_2^+ signal were due solely to trimers. They also commented that the signal might be consistent with the equilibrium population of dimers. However, they did not claim to know the actual neutral beam composition, and they gave no information on the beam temperature to permit the composition to be estimated. Interestingly, the pressure dependence of the

 0021-9606/94/100(5)/4023/2/$6.00

He_2^+ signal in the SK experiments changes from an exponent of 3 to a value substantially *higher* than 3, just at the point where the He_3^+ signal becomes detectable. This suggests an additional contribution to the He_2^+ signal from the same specie(s) responsible for the He_3^+ signal, which may have been clusters larger than He_3.

(iv) The preceding point notwithstanding, there is a simple reason why one should expect the branching ratio to be small for survival of a weakly-bound trimer to produce the corresponding trimer ion. Since the binding energy is greater and the internuclear distances smaller in the trimer ion than in the neutral, vertical ionization will generally deposit substantial amounts of energy in all three vibrational modes. This energy will be rapidly pooled, and will result in dissociation if the total excitation energy exceeds the trimer ion dissociation energy. However, the branching ratio for survival of the dimer as the dimer ion is *not* expected to be small because there is only one vibrational degree of freedom in each of these species. Thus, Buck and Meyer[10] found the branching ratio for $Ar_2 \rightarrow Ar_2^+$ to be 0.6. While poorer Franck–Condon factors are likely to make the $He_2 \rightarrow He_2^+$ branching ratio considerably smaller than this, it is certainly reasonable to expect He_2 to be detectable as He_2^+ in our experiments. In fact, the quasiequilibrium calculation for the He_2/He density ratio mentioned by MMS agrees with our measured I_8/I_4 ratios if one takes the $He_2 \rightarrow He_2^+$ branching ratio to be 0.03 and the ratio of ionization cross sections for the dimer and monomer to be two. The branching ratio of 0.03 derived from this assumption is certainly of the expected order of magnitude.

(v) The binding energies of $^4He_3$ and $^4He_2$ ^3He quoted by MMS[11] are based on the 1970 dimer potential of Bruch and McGee[12] which has a well depth of 10.75 K. This well depth is 0.26 K smaller than the best current estimate,[13] which makes the quoted trimer binding energies too low as well. It is therefore difficult to estimate what population of $^4He_2$ ^3He might have been present under our experimental conditions. We included data on mixed ^4He–^3He beams in our original paper because the observation of a $^4He^3He^+$ signal would have been definitive evidence of the presence of clusters larger than the dimer. However, we agree with MMS that the absence of the I_7 signal does not by itself constitute proof that the I_8 signal comes from He_2. As we stated in the original paper and reiterate above, the principal support for that conclusion comes from the pressure dependence measured under conditions where all signals from species other than He_2^+ are negligible.

We appreciate the opportunity provided by this Reply to expand on the basis for our conclusion that we have detected bound $^4He_2$ for the first time. Even though we find the arguments made by MMS not to be supported by the evidence, the issues which they raise are ones which must be considered. Also, of course, independent experiments are needed not only to confirm the existence of $^4He_2$, but to characterize the structure and dynamics of this very special molecule. We are pursuing such experiments now.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grants Nos. CHE-8705611 and CHE-9223195.

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[1] E. S. Meyer, J. C. Mester, and I. F. Silvera, J. Chem. Phys. **100**, 4021 (1994).
[2] A. P. J. van Deursen and J. Reuss, J. Chem. Phys. **63**, 4559 (1975).
[3] P. W. Stephens and J. C. King, Phys. Rev. Lett. **51**, 1538 (1983).
[4] F. Luo, G. C. McBane, G. Kim, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993).
[5] J. Wang, V. A. Shamamian, B. R. Thomas, J. M. Wilkinson, J. Riley, C. F. Giese, and W. R. Gentry, Phys. Rev. Lett. **60**, 696 (1988).
[6] U. Buck, J. Phys. Chem. **92**, 1023 (1988).
[7] D. R. Miller, *Atomic and Molecular Beam Methods*, Vol. 1 (Oxford University, New York, 1988), Chap. 2; M. Kappes and S. Leutwyler, *ibid.*, Chap. 15.
[8] F. Luo, G. Kim, G. C. McBane, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 9687 (1993); F. Luo, G. Kim, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **99**, 10086 (1993).
[9] S. Nakaichi-Maeda and T. K. Lim, Phys. Rev. A **28**, 692 (1983).
[10] U. Buck and H. Meyer, J. Chem. Phys. **84**, 4861 (1986).
[11] H. S. Huber and T. K. Lim, J. Chem. Phys. **68**, 1006 (1978); K. Duffy and T. K. Lim, J. Chem. Phys. **70**, 4778 (1979).
[12] L. W. Bruch and I. J. McGee, J. Chem. Phys. **52**, 5884 (1970).
[13] J. B. Anderson, C. A. Traynor, and B. M. Boghosian, J. Chem. Phys. **99**, 345 (1993).