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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

INCHAN CHOI

ENTITLED NUCLEAR QUADRUPOLE COUPLING INTERACTION AT MOLYBDENUM (V) CENTERS.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

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Instructor in Charge

APPROVED: John C. [illegible]

for **HEAD OF DEPARTMENT OF** CHEMISTRY

O-1364

NUCLEAR QUADRUPOLE COUPLING INTERACTION AT MOLYBDENUM (V) CENTERS.

BY

INCHAN CHOI

THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

College of Liberal Arts and Sciences

University of Illinois

Urbana, Illinois

1985

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ACKNOWLEDGEMENT

I would like to thank Prof. R. Linn Belford for allowing me to taste the joy of scientific research. Very special thanks to Dr. Mark Nilges for Q-band, to Kurt Rothenburger for X-band spectra, and to Jeff B. Correlius for computer simulation. Quadruple (or Quadrupole) thanks to Jeff and Kurt again for their patience with my limitless questions.

I. INTRODUCTION

1. Introduction

In the early 1930's Bleaney[1~3] suggested that the nuclear quadrupole coupling interaction could be studied with EPR. So and Belford[4,5] examined the secondary (or forbidden $\Delta M_I = \pm 1$) transitions in the single crystal EPR spectra for several copper-oxygen complex and they developed systematic methods for extracting quadrupole coupling information from EPR spectra of magnetically dilute oriented single crystals. Later, Belford's group extended methods employed in these studies to frozen solutions and powder samples.[6~9]

The quadrupole coupling arises from the electrostatic interaction between a quadrupolar nucleus, which has a nuclear spin $I \geq 1$ and thus a nonspherical nuclear charge distribution, and its electronic environment, which in turn is determined primarily by the electrons and the nuclei in the vicinity of the quadrupolar nucleus. The quadrupole coupling constant, $eq \cdot eQ$, is the product of the quadrupole moment of the nucleus, eQ, and the major electric field gradient, eq. The moment, eQ, is a measure of the anisotropic distribution of the charge within the nucleus. The gradient, eq, is a measure of the anisotropic distribution of the charge surrounding that nucleus.[10~12]

The orientation of the quadrupole moment is inherently defined by the orientation of the nuclear magnetic moment. The nuclear magnetic moment is aligned with an effective magnetic field defined by the external magnetic field, the hyperfine tensor, and the quadupolar tensor. When an electron spin flip is induced in the EPR experiment, the new wave functions are linear combination of the old wavefunctions and they result in small amount of "allowed" transitions which appear as "forbidden" transitions. Therefore, the quadrupole coupling interaction has three major effects on the EPR spectra; (1) the enhancement of the intensity of the "forbidden" transition, (2) the change of line position of "forbidden" transitions with the magnetic field orientation, (3) the change of line positions of "allowed" transitions.

In a recent work, Licswek[13] reported that the value of the nuclear quadrupole coupling constant of tetrakis (N,N-diethyl-dithiocarbamato) molybdenum (V) cation,$Mo(Et_2dtc)_4^+$, was almost zero. This rather surprising result was questioned by Maurice[14] who reports in his study of molybdenum (V) ions that the optimum value of the quadrupol coupling constant is 6.5 MHz. The conflicting results of Licswek and Maurice prompted me to investigate the nuclear quadrupole coupling at Molybdenum (V) centers.

In this study, I designed three experiments; (1) the synthesis of tetrakis (N,N-diethyldithiocarbamato) molybdenum (V) chloride and the study of its frozen solution EPR spectra (2) the computer simulation of Licswek's and Maurice's spectra, (3) the synthesis of another molybdenum (V) complex and the study of its EPR spectra. However, the third experiment, which would have provided corroborating evidence for one of the results, the synthesis of oxochloromolybdenum (V) tetraphenylporphyrin, could not be completed given the limitations in time and the difficulty in the synthesis of oxochloromolybdenum (V) tetroporphyrin. A brief report of the synthesis is included in Chapter II.

2. The experimental results of Liczwek and Maurice

Liczwek[13] studied nuclear quadrupole coupling at eight coordinate Mo(V) centers. Liczwek used ^{92}Mo, ^{95}Mo, and ^{97}Mo in the preparation of three enriched compounds of Mo $(Et_2dtc)_4Cl$ and the frozen solution spectra of the enriched compounds in ethanol were recorded at X, Q, and S-bands. These spectra were then simulated and analyzed in the University of Illinois CDC Cyber 175 computer and VAX/VMS 11/780 computer.

Liczwek reports that (1982, p. 127);

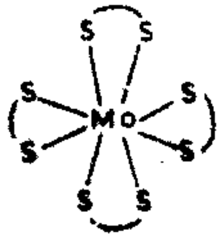
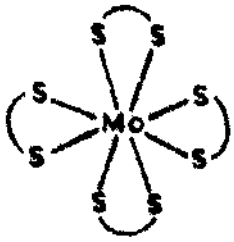
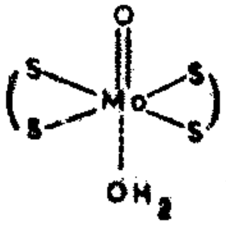
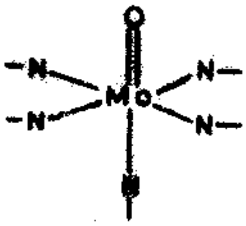
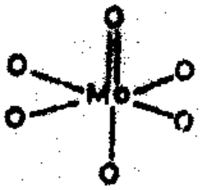
> Surprisingly, the X-band spectrum shown in Figure 39 (the X-band spectrum of ^{97}Mo Figure 14 in this study) displayed no quadrupolar effects, when compared with the X-band of the ^{95}Mo analog. . . . The features of the ^{95}Mo and ^{97}Mo compounds are the same, no extra peaks are seen which are due to nuclear quadrupole interactions nor is there a noticeable change in intensity of the peaks. Obviously, then the nuclear quadrupole coupling constant for $Mo(dtc)_4^+$ cation is some value near zero.

Maurice[14] induced a reaction of poly (iminoethylen) dithiocarbonate copolymer with molybdenum trioxide in an acidified solution. Part of the product he obtained had some molybdenum ions bound to basic nitrogen as polymolybdate ions while some molybdenum ions had been reduced and were bound to the sulphure of a dithiocarbonate group as expected. The EPR spectra of the latter species were consistent with a structure in which each molybdenum (V) was bound to four dithiocarbonate groups, analogous to that of the complex ion [Mo $(Et_2NCS_2)_4$]. He reported in his study that ^{97}Mo spectrum contained a significant quadrupole contribution and he obtained an optimum value of the quadrupole coupling constant of 6.5 MHz. He explains the possible reason for the difference between Licswek's result and his in the following manner: (1982, p. 97)

> The magnitude of the quadrupole coupling seems to be dependent upon the ligand-barring the second complex in Figure 17 (Figure 1 in this report). The absence of any quadrupole in the second complex (Licswek's complex) may be due to a reduction of the field gradient through symmetry.

Figure 1. Proposed structure for Mo (V) sites in the copolymer along with the known structures for the only four other molybdenum (V) complexes for which EPR studies have been conducted. The EPR parameters for ^{97}Mo are shown for comparison. The hyperfine and quadrupole parameters are in MHz.

* from reference 14

	g_x	g_y	g_z	a_x	a_y	a_z	QD	Ref.
	1.9800	1.9800	1.9760	69.4	76.0	174.9	6.5	(this work)
	1.9808	1.9835	1.9797	76.5	70.5	172.5	0.0	(60)
	1.9810	1.9790	2.0500	61.5	61.5	147.5	6.0	(58)
	1.9441	1.9393	1.9288	96.9	97.7	210.6	3.0	(24)
	1.9368	1.9340	1.9108	96.5	96.5	221.2	9.0	(58)

II. SYNTHESIS

1. Synthesis of Tetrakis (N,N-Diethyldithiocarbamato) Molybdenum (V) Chloride

Introduction

Nieuwpoort[15] developed a very simple synthesis of tetrakis (N, N-diethyldithiocarbamato) molybdenum (V) chloride: $[Mo(Et_2dtc)_4]Cl$. By heating tetrabutyl ammoniumchloride and molybdenum hexacarbonyl in distilled diglyme, he obtained a solution containing tetrabutylammonium pentacarbonyl chloromolybdate (0).[16] He reported that when tetraethylthiuramdisulphide is added to this solution $[Mo(Et_2dtc)_4]Cl$ can be produced.

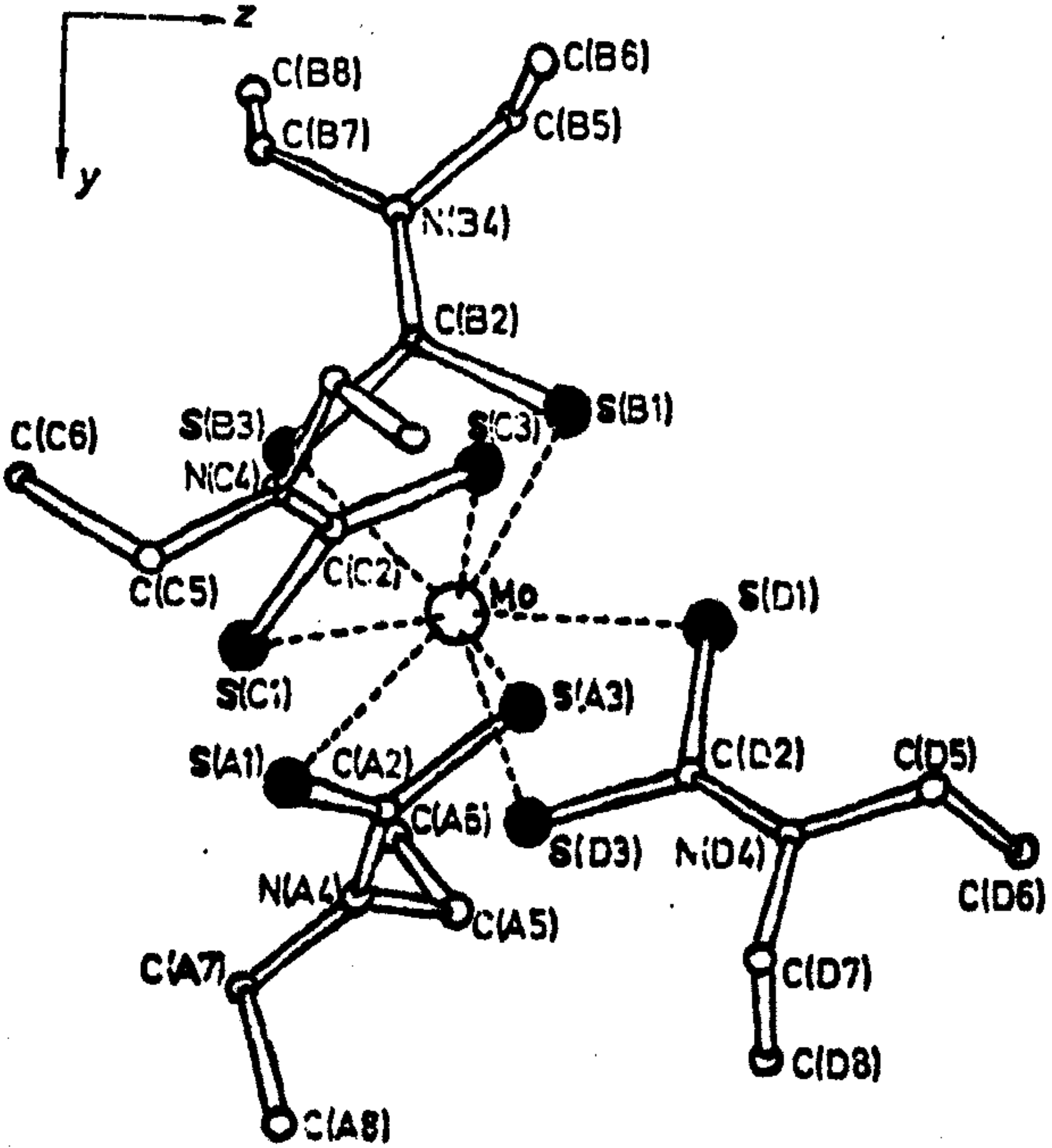
Experimental

All reagents were obtained commercially (tetrabutylammoniumchloride: Pfaultz and Bauer; molybdenum hexacarbonyl: Stern Chemical Co.; tetraethylthiuramdisulphide, diglyme, acetone, and diethyl ether: Aldrich). Diglyme was distilled prior to use. All other reagents were used as received. The elemental analyses were performed by the University of Illinois micro-analytical laboratory. The IR spectrum was obtained on a Perkin-Elmer 281 infrared spectrophotometer.

Since the reaction involves the evolution of CO gas, the system was set up in the hood. A 100 ml round bottom flask containing a magnetic stirring bar was connected to a bubler. To the flask, tetrabutylammonium chloride (0.8417 g, 3.0 m mol) and $Mo(CO)_6$ (0.8184 g, 3.1 m mol) were added. Then distilled diglyme (10 cm^3) was added. In

Figure 2. Crystallographic drawing of molybdenum tetrakis (N, N-diethyldithiocarbamato) chloride, $Mo(Et_2dtc)_4$

* From reference 13.


z
y
C(B8)
C(B6)
C(B7)
C(B5)
N(34)
C(B2)
S(B1)
C(C6)
S(B3)
S(C3)
N(C4)
C(C2)
C(C5)
Mo
S(D1)
S(C1)
S(A3)
S(A1)
C(A2)
C(D2)
C(D5)
C(A6)
S(D3)
N(D4)
C(D6)
N(A4)
C(A5)
C(A7)
C(D7)
C(D8)
C(A8)

an oil-bath, the solution was at a bath temperature of 100°C while being stirred. While the reaction was being completed, the pale yellow color of the solution changed to red-brown and CO gas evolution continued. After an hour of reaction time, the evolution of CO gas stopped and the flask was removed from the oil bath. To the hot solution, tetraethyl thiuram disulphide (2.2241 g, 7.5 m mol) was carefully added. This resulted in a fast oxidation reaction. After cooling the solution to room temperature, the red-brown fudge-like compound was isolated by suction filtration and washed thoroughly with diethylether. This product was characterized as [Mo(Et$_2$dtc)$_4$]Cl (1.4127 g, 1.95 m mol, 65.0%). Anal. Calcd for $C_{20}H_{40}$ N_4S_8MoCl: C, 33.2; H, 5.5; N, 7.7. Found: C, 35.12; H, 6.05; N, 7.16. Further purification was accomplished by recrystallization. The product was dissolved in a minimum amount of hot acetone and the solution was filtered while hot. To the filtrate, the same amount of diethyl ether was added. The solution was concentrated on a rotary evaporator. The crystals were suction filtered and washed completely with diethyl ether. These crystals were characterized as [Mo(Et$_2$dtc)$_4$]Cl (0.8476 g, 1.67 m mol, 60%). Anal. Calcd for $C_{20}H_{40}N_4S_8$MoCl: C, 33.2; H, 5.5; N, 7.7; S, 35.4; Mo, 13.3; Cl, 4.9. Found: C, 32.80; H, 5.50, N, 7.48; S, 34.93; Mo, 12.87; Cl, 5.18.

IR data of [Mo(Et$_2$dtc$_4$)Cl are summarized in Table I.

Results and Discussion

The synthesis was straightforward and simple. The product was readily and usefully analyzed by the elemental analysis and IR. The elemental

Table I

IR Spectra Data of the compound $Mo(Et_2dtc)_4$ Cl.

Experimental		Literature[17]		Assignment
$\bar{\nu}$ (cm^{-1})	intensity	$\bar{\nu}$ (cm^{-1})	intensity	
1520	very strong	1519	very strong	CN
1210	strong	1208	strong	NC_2
-	-	1016	very weak	
1000	weak	1001	weak	CSS
610	medium	611	medium	

* The IR spectra were in KBr pellet.

analysis indicated that the product was essentially pure [Mo(Et_2dtc)$_4$]Cl after recrystallization. The IR data appeared to be in agreement with the data from the literature. The yield was good.

[Mo(Et_2dtc)$_4$]Cl is a red-brown crystal compound. It is very soluble in ethanol and chloroform, less soluble in acetone and nitrobenzene, hardly soluble in water, and insoluble in benzene and diethyl ether. It is stable toward air and water but in solvents, it seems to be susceptive to influence from the impurities in the solvents. This versatile nature makes the recrystallization very difficult. A good recrystallization is obtained when the mixture of acetone and diethylether is used as solvents.

2. Synthesis of Oxochloro Molybdenum (V) Tetraphenylporphine

Introduction

Lendon and Mentzen[18] reported a modified synthesis of oxochloromolybdenum(V) tetraphenylporphyrin: O=Mo(TPP)Cl. Refluxing tetraphenylporphine (abbreviated subsequently as TPP) with $Mo(CO)_6$ in anhydrous and oxygen-free decalin and octane yield MoO(OH)TPP. When this product was chromatographed over alumina and eluted with CH_2Cl_2, O=Mo(TPP)Cl, a versatile intermediate in the coordination chemistry of molybdenum porphyrins, was prepared.

Experimental

All reagents were obtained commercially (tetraphenylporphine, decalin, octane, dichloromethane, and hexane: Aldrich; molybdenum hexacarbonyl: Stern Chemicals Inc.). Decalin and octane were dried from sodium under nitrogen prior to use. All the other reagents were used as received. The IR spectrum was obtained on a Perkin-Elmer 281 infrared spectrophotometer. The elemental analysis was performed by the University of Illinois microanalytical laboratory.

@ Synthesis of O=Mo(TPP)Cl.

A 500 ml 3-neck round bottom flask containing a magnetic stirring bar was fitted with a nitrogen inlet and a water-cooled condenser. The side arms were capped with a serrum rubber stopper and a glass stopper. TPP (3.12 g, 5 m mol) and $Mo(CO)_6$ (6.6 g, 25 m mol) was added to the flask and the system was flushed with nitrogen for 5 min. Then, anhydrous and oxygen-free decalin (200 ml) and octane (50 ml) were added through a serrum stopper by a cannula. While being stirred, the mixture was refluxed under nitrogen over a period of two hours. After the solution was cooled to room temperature, a dark blue crystalline precipitate was collected by suction filtration and thoroughly washed with pentane. The unreacted $Mo(CO)_6$ was removed by vacuum sublimation at 80°C. This intermediate product was dissolved in CH_2Cl_2 and the solution was passed through a column packed with dry alumina ("Aluminum Oxide", activity 1, 250 g.). The column was eluted with CH_2Cl_2 and the deep-brown effluent was evaporated on a rotary evaporator. Then, hexane (200 ml) was added to the solution and the solvent was again evaporated until crystals were visible. The dark-green crystalline was collected by suction filtration and dried under vacuum at 100°C, over night (0.2283 g, 0.3 m mol, 6.0%).

Table II

IR Spectra Data of the MoO(TPP)Cl.

Experimental		Literature[7]		Assignment
$\bar{\nu}$ (cm^{-1})	Intensity	$\bar{\nu}$ (cm^{-1})	Intensity	
905	weak	971	medium	O=Mo Vibration
640	very strong	648	strong	O=Mo Vibration
610	strong	614	strong	O=Mo Vibration

Anal. Calcd. for $C_{44}H_{28}ClMon_rO$: C, 69.53; H, 3.71; Cl, 4.66; Mo, 12.62; N, 7.37. Found: C, 70.78; H, 4.08; Cl, 0.89; Mo, 11.43; N, 7.11. IR data are summarized in Table II.

Results and Discussion

This compound is highly susceptive to impurities in solvents, air, and water and this made its synthesis very challenging. The solvents, decalin and octane, were dried over sodium under nitrogen over a period of 48 hrs. Because of the high boiling points of solvents, a large heating mantle was used, and the reaction flask was covered with sand while the mixture was being refluxed.

The intermediate product, MoO(OH)TPP, was prepared without much difficulty. However, O=Mo(TPP)Cl was not as easily obtained as Landon and Mentzen[18] had reported. In the elemental analysis of the final product, it was found that only 21% of it contained chlorine. In this study, the rest was assumed to obtain hydroxide. The support for this assumption comes from the similarities in the preparation method employed by Srivastava and Fleischer[19] in the preparation of MoO(OH)TPP, and that employed in the present study as well as from the IR spectra evidence.

The yield was significantly lower than the 63.5% reported by Landon and Mentzen.[18] The IR spectrum of the final product showed three additional bands in the region (4000 600 cm^{-1}) as compared to the TPP spectrum. These bands were 905 (weak), 640 (very strong), and 610 (strong), and were due to Mo=O vibrations.

In conclusion it seemed that the preparation method by Lendon and Mentzen[18] did not prove to be very successful. The method seemed to be lacking in some specific details of execution. Due to limitations of time, a different method of preparation was not attempted.

III. EPR STUDY

Experimental

X-band EPR studies were carried out on a Varian E-9 spectrometer at the University of Illinois. It operates in the range 9.1 to 9.5 GHz. The X-band frequency was determined with a Hewlett-Packard Model 5260 A 12.4 GHz digital frequency meter. The exact magnetic field was determined with a Brucker BNM20 magnetometer. Q-band EPR studies were performed on a Varian E-9 spectrometer operating in the vicinity of 35.0 GHZ with an E-110 microwave bridge and an TE011 wavemeter mode cavity. The frequency for Q bands was determined with a Hewlett-Packard Model 5260 A digital frequency meter.

Frozen solution spectra were recorded at X-band in three solvents with differing degree of their coordinating ability: pyridine, ethanol, and dimethylformamide. All solutions were dried from activated molecular sieves for a period of 48 hours. For simplicity, the Q band study was carried out in ethanol. All samples were quickly frozen by immersion in liquid nitrogen. In both the X and Q-band experiments, samples were held in a quartz Dewar in a cold nitrogen stream in the standard Varian variable temperature apparatus.

2. Calculations

Calculations utilized the University of Illinois School of Chemical Sciences VAX VMS 11/780 computer to simulate spectra plotted on a

Houston Instrument Hiplot Plotter. The program used in this study is a modification of QPOW[20 22], a program which does EPR simulations. QPOW has been described briefly by Nilges and Belford.[20]

The modified version employed in this study simulates the EPR spectra of systems whose electron spin, S, is 1/2 and the nuclear spin, I, is less than 7/2. Further details are in the comment statements of the program.[20-24]

3. Results and Discussion

Naturally Abundant Molybdenum Spectrum.

Naturally occurring molybdenum contains 75% even isotopes with nuclear spins of zero. Because of the small anistropy in the g matrix, these isotopes appear as a single peak. The isotopes, ^{95}Mo and ^{97}Mo which are also present, form several less intense peaks. The computer simulation of this spectrum consisted of computing several isotopically pure simulations and summing them together, weighted by their abundance.

Figure 3 shows the X-band spectrum of natural abundance molybdenum in $Mo(Et_2dtc)_4Cl$ and its corresponding computer simulation. The Q-band spectrum and its simulation is shown in Figure 4. The parameters which generate the simulation are listed in Table IV.

Both Q-band and X-band spectra contained noticeable quadrupole contributions. This is not surprising since c.a. 9.5% of the sample consisted of ^{97}Mo whose nucleus contains an appreciable quadrupole moment. A comparison of Figures 5(a) and 5(b) should illustrate the effect of inclusion of a quadrupole coupling interaction. The optimum value of the quadrupole constant was 4.0 MHz.

Figure 3. Experimental and simulated X-band spectra for naturally abundant Mo(Et$_2$dtc)$_4$Cl in ethanol. (Best fit parameters listed in Table III). Experimental parameters; frequency, 9.101 GHz; power, 1 MW; gain, 1.25×10^3 ; modulation amplitude, 0.50 Gauss, time constant, 0.3 sec.

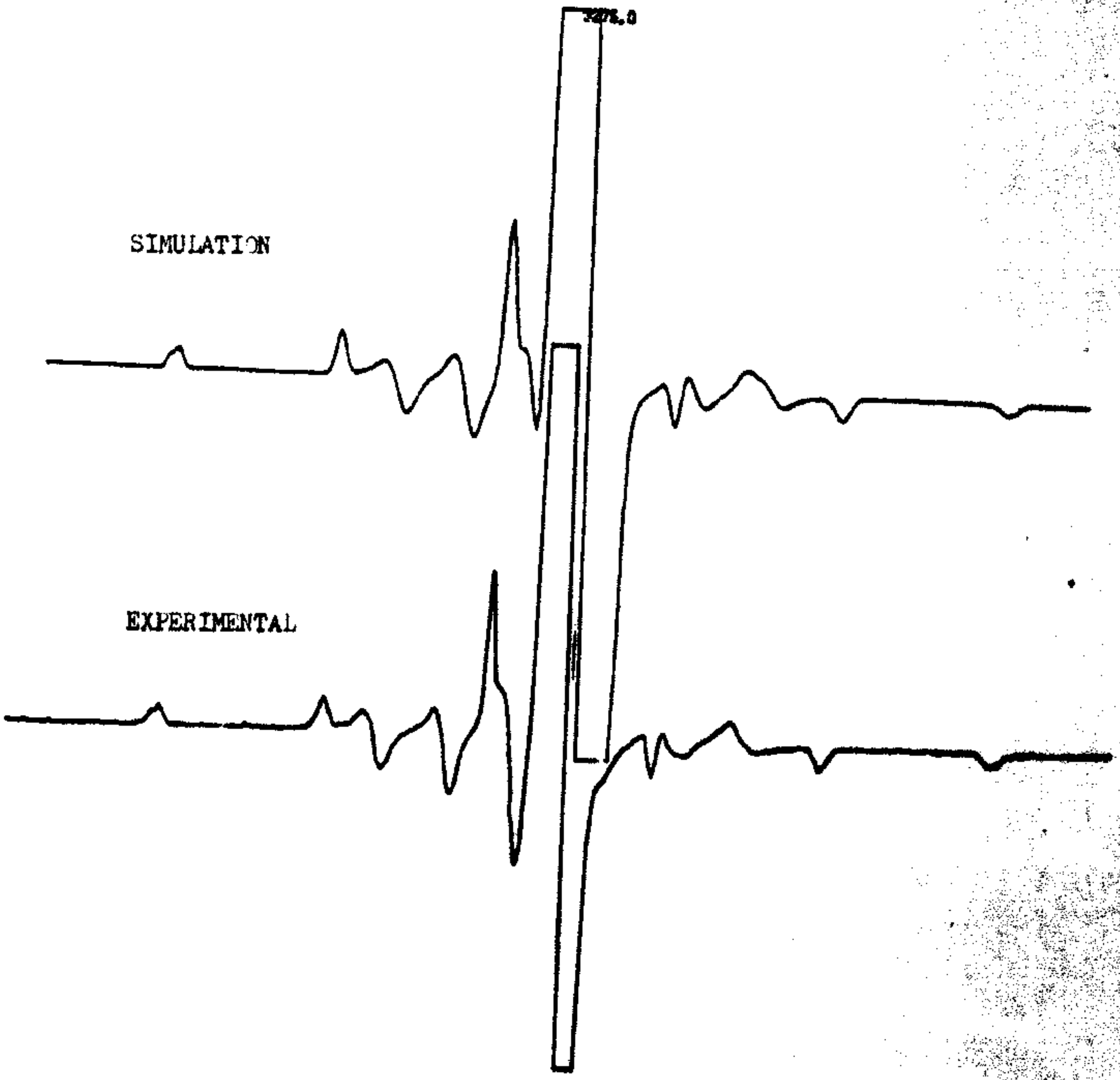

SIMULATION
EXPERIMENTAL

Figure 4. Experimental and simulated Q-band spectra for natural abundance $Mo(Et_2dtc)_4Cl$ in ethanol. (Best fit parameters listed in Table III). Experinmental parameters: frequency, 35.060 GHz; power 1 MW; gain, 4.0 x 10^2; modulation amplitude, 2.0 Gauss; time constant, 0.3 sec.

➡ is TPPH contamination.

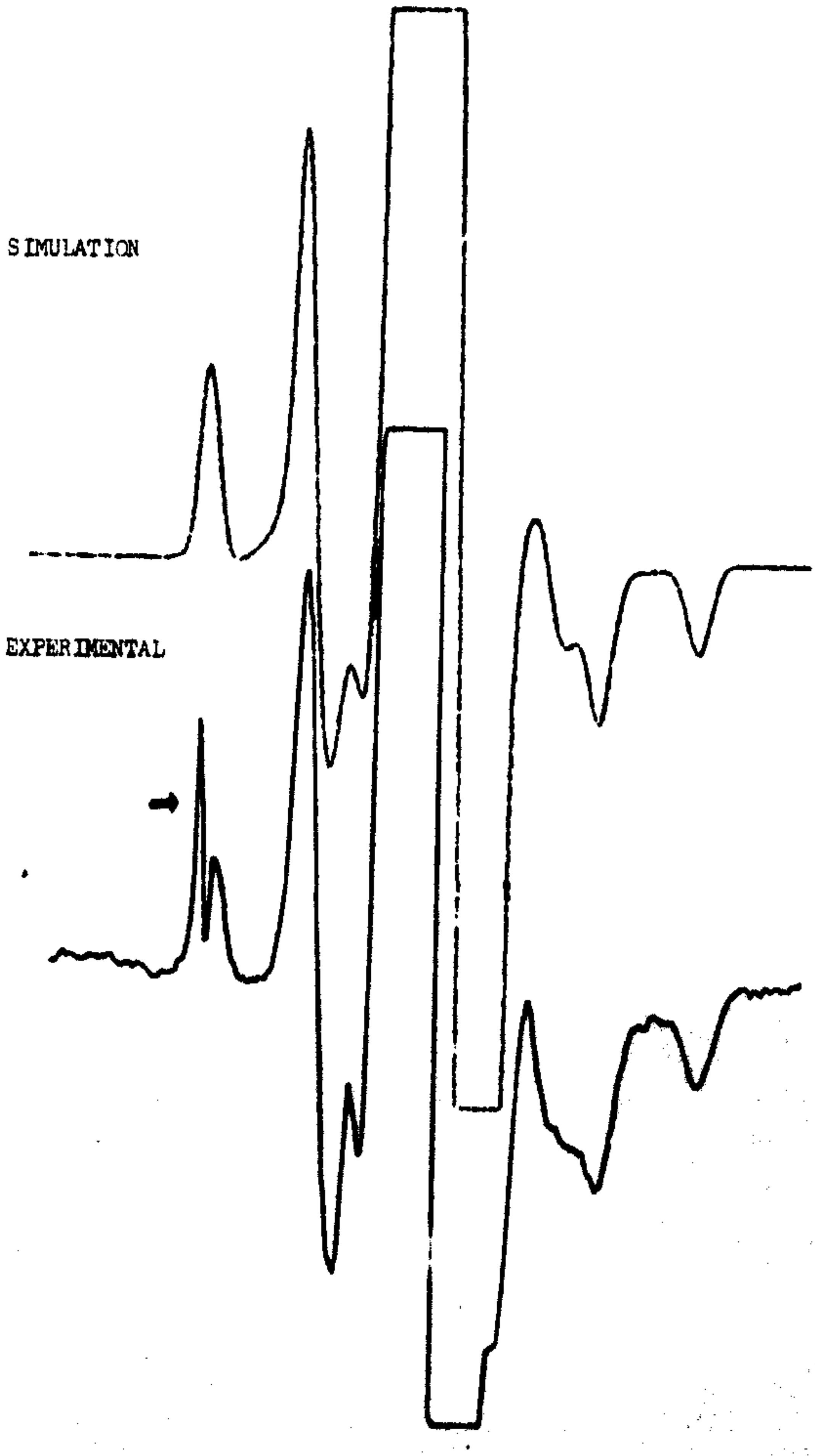

SIMULATION
EXPERIMENTAL

Table III

Parameters Used in Computer Simulation of Naturally Abundant Mo EPR Spectra [a]

	Q-band	X-band
Freq.[b]	35.06	
g_x	1.908	1.9080
g_y	1.9835	1.9835
g_z	1.9797	1.9797
A_x	- 76.54	- 76.34
A_y	- 70.46	- 70.46
A_z	- 172.58	- 172.58
QD	4.0	4.0
x	2	2.0
y	2	2.0
z	- 1.5	- 1.5
C_{1x}	0.5	0.5
C_{1y}	0.5	0.5
C_{1z}	1.5	1.5
C_{2x}	0.7	0.7
C_{2y}	0.7	0.7
C_{2z}	0.6	0.6

[a] Hyperfine and quadrupole values are in MHz.

[b] Frequencies are in GHz.

Figure 5 a) Simulation of natural abundance molybdenum. All quadrupolar interactions have been deleted.

b) Simulation with identical parameters as in a), except for the inclusion of quadrupole. QD is set at 4.0 MHz.

* X-Band Spectra.

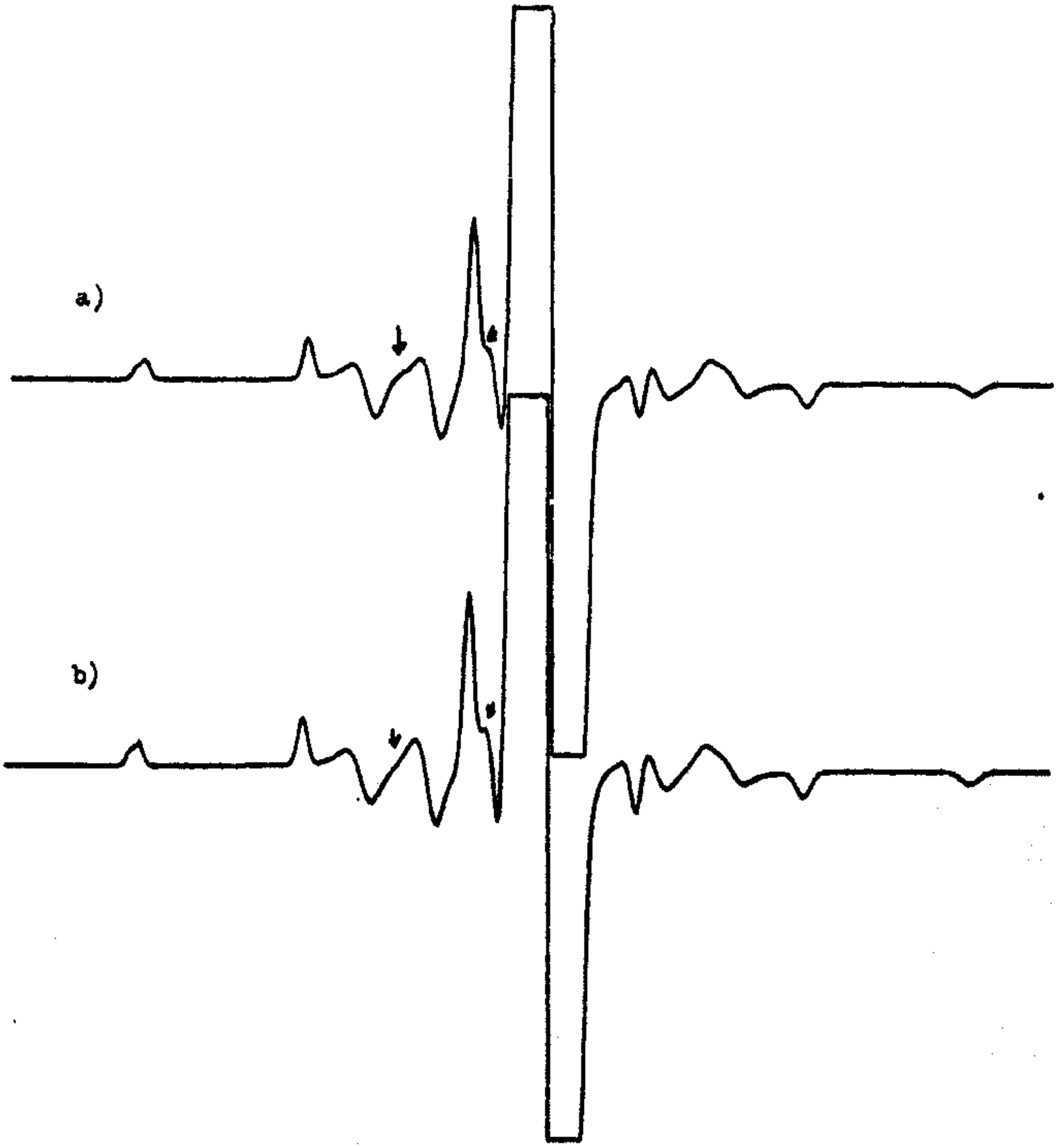
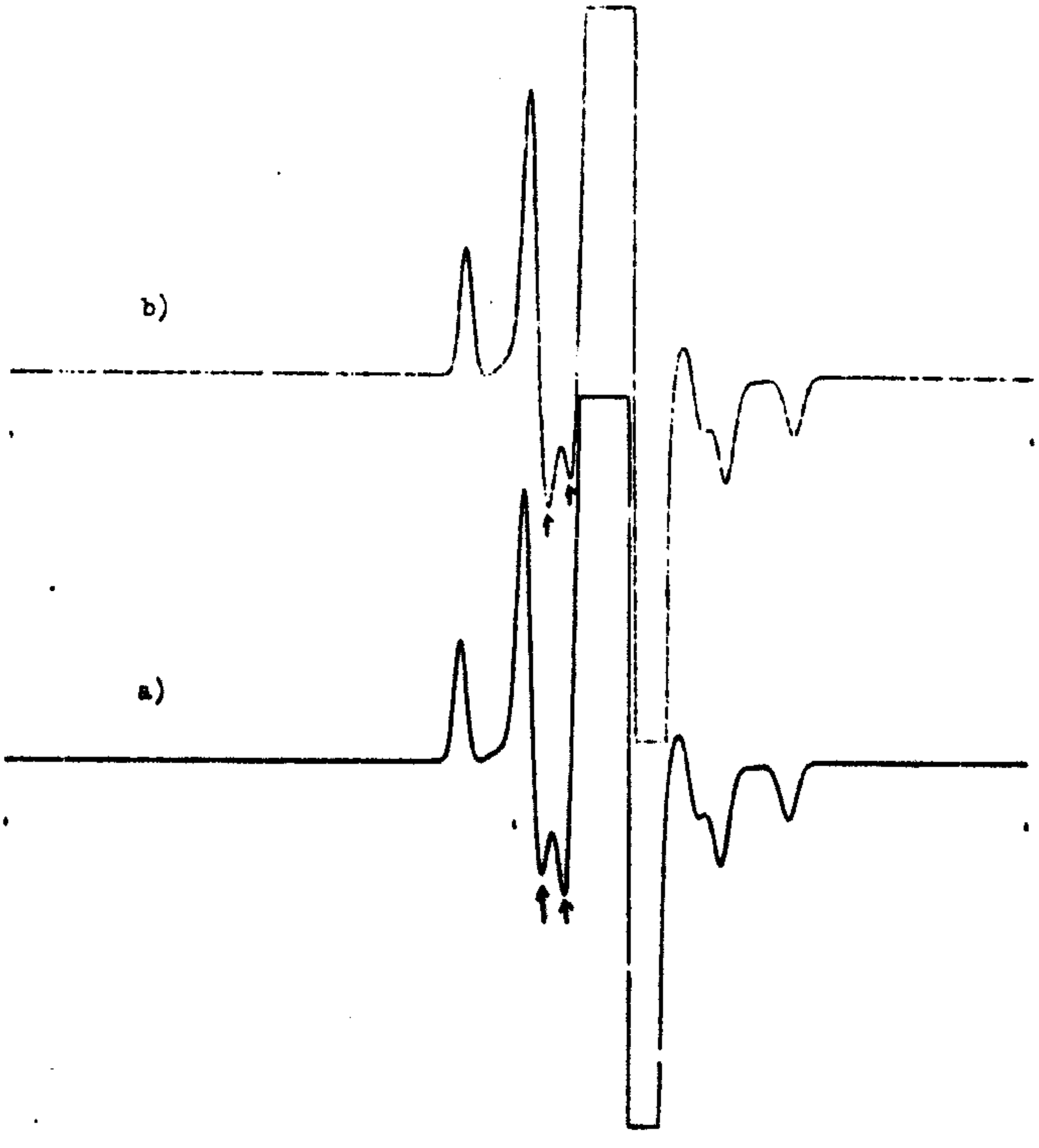

a)
b)

Figure 6. a) Simulation of natural abundance molybdenum Q-band spectra. All quadrupolar interaction have been deleted.

b) Simulation with identical parameters as in a), except for the inclusion of quadrupole. QD is set at 4.0 MHz.


b)
a)

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^{95}Mo Spectrum

Figure 7 shows the isotropically enriched ^{95}Mo X-band spectrum with its corresponding computer simulation done by Liczwek. Figure 8 shows Liczwek's ^{95}Mo X-band spectrum and its simulation done in the present study. Figure 9 shows the difference between the simulation with (a) and without (b) quadrupole. The parameters pertinent to the simulation are listed in Table IV. No quadrupole was found to be necessary for the simulation, consistent with what Liczwek[13] and Maurice[14] reported, since the quadrupole moment of this compound is very small; c.a. 0.01.

^{97}Mo Spectrum

Figure 10 shows Liczwek's ^{97}Mo Q-band with its simulation done for the present study. Figure 11 shows Maurice's ^{97}Mo X-band and its simulation. Figure 12 shows Liczwek's ^{97}Mo X-band and its simulation. In contrast to the ^{95}Mo specturm, these spectra contain significant quadrupole contributions. This is surprising in view of Liczwek's results but not when one considers the fact that a ^{97}Mo nucleus contains an appreciable quadrupole moment. The difference between the result of the simulation done in this study and Liczwek's may be due to Liczwek's failure to recognize the effect of the quadrupole coupling in her simulations. In addition, the present results are consistent with Maurice's[14] and with the spectra of naturally abundant molybdenum simulated in this study. Figure 13 shows the ^{97}Mo Q-band spectrum with its simulation by Liczwek. The difference between the spectra and the simulation can be noticed (see the arrow). By comparing Figures 10 and 13, one can

Figure 7. Experimental and simulated X-band spectra for ^{95}Mo by Liczwek[13].

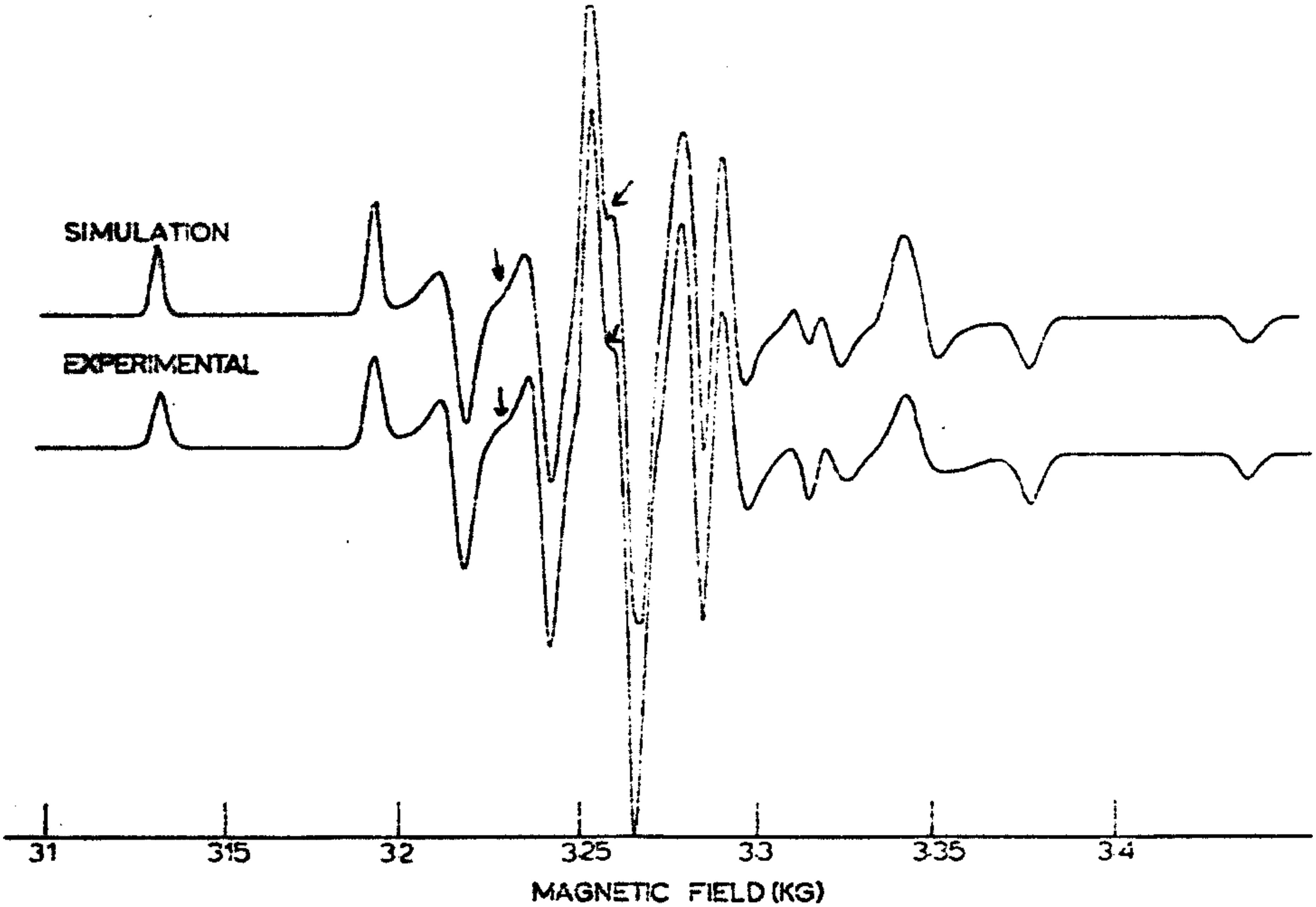

SIMULATION
EXPERIMENTAL
3·1
3·15
3·2
3·25
3·3
3·35
3·4
MAGNETIC FIELD (KG)

Figure 8. Simulation of Liczwek's ^{95}Mo X-band spectrum. (Best fit parameters are listed in Table IV).

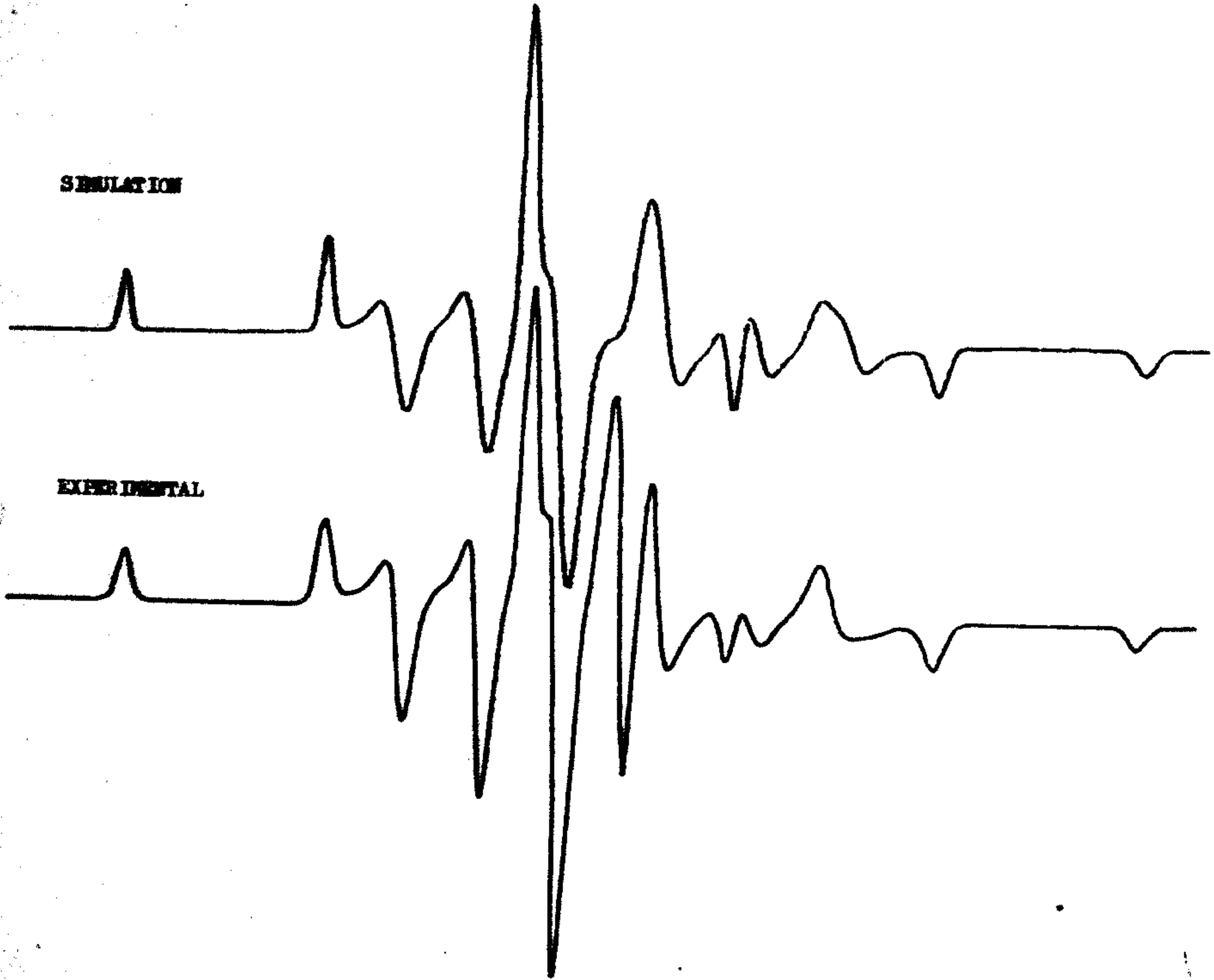

SIMULATION
EXPERIMENTAL

Figure 9. Simulation of ^{95}Mo X-band spectrum a) with QD 6.5 MHz, b) without QD.

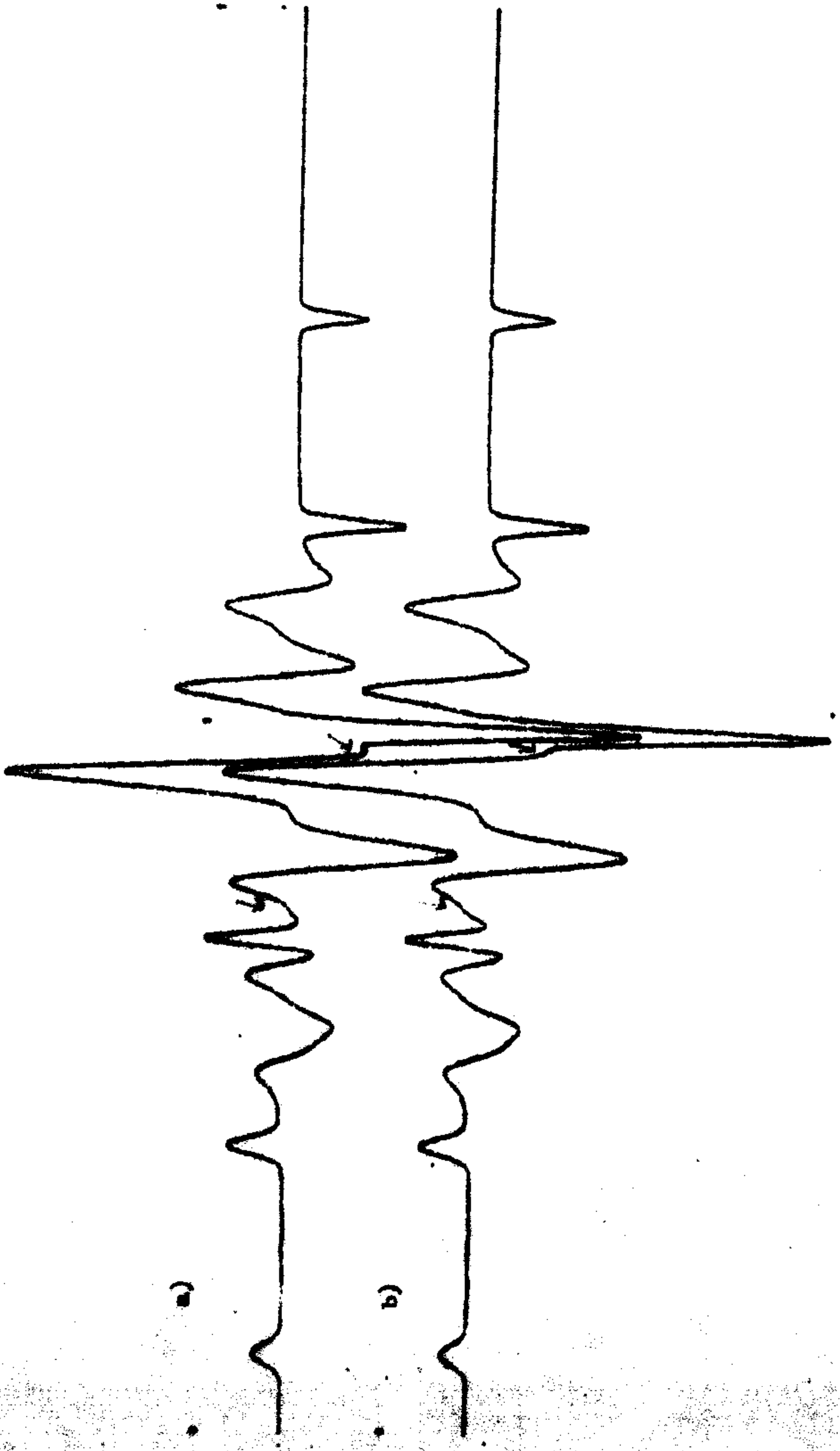

a)
b)

Table IV

Parameters Used in Computer Simulation of Enriched Mo EPR Spectra[a]

	^{95}Mo	^{97}Mo	
	Liczwek's spectra	Liczwek's spectra	Maurice's spectra
Freq.[b]	9.1015	9.1171	9.1015
g_x	1.9808	1.9800	1.9808
g_y	1.9835	1.9800	1.9835
g_z	1.9797	1.9760	1.9797
A_x	- 76.54	- 69.4	- 76 .4
A_y	- 70.46	- 76.0	- 70.46
A_z	- 172.58	- 174.9	- 172.58
QD	0.0	4.0	4.0
x	2.0	- 3.0	2.0
y	2.0	- 3.0	2.0
z	- 1.5	- 9.0	- 1.5
C_{1_x}	0.5	1.33	0.5
C_{1_y}	0.5	1.33	0.5
C_{1_z}	1.5	1.33	1.5
C_{2_x}	0.7	1.5	0.7
C_{2_y}	0.7	1.5	0.7
C_{2_z}	0.6	1.5	0.6

[a] Hyperfine and quadrupole values are in MHz.

[b] Frequencies are in GHz.

Figure 10. Simulation of ^{97}Mo Q-band spectrum. (Best fit parameters listed in Table IV).

* Experimental Spectrum was obtained by Liczwek[13].

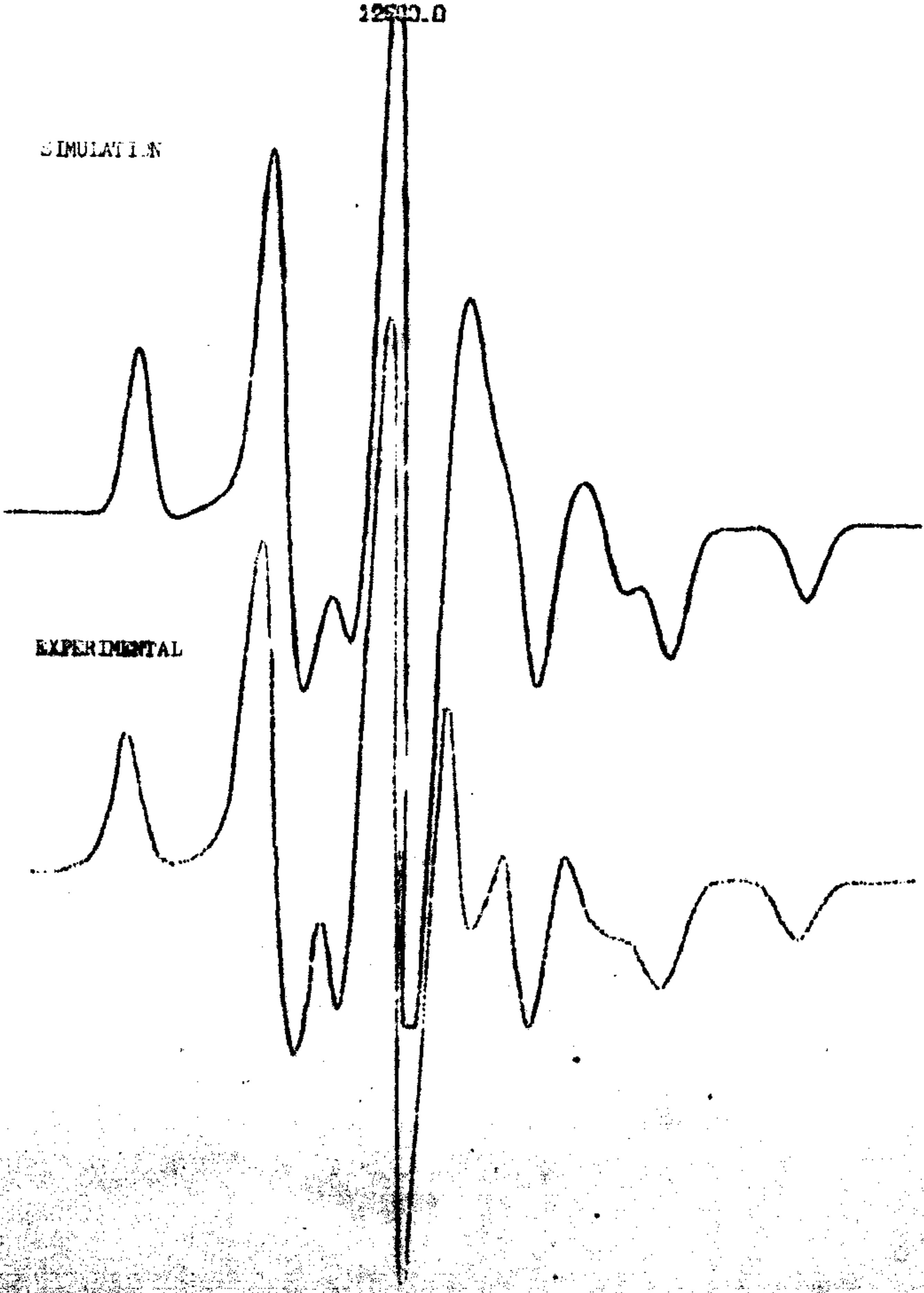

12500.0
SIMULATION
EXPERIMENTAL

Figure 11. Simulation of Maurice's ^{97}Mo X-band spectra. (Best fit parameters listed in Table IV).

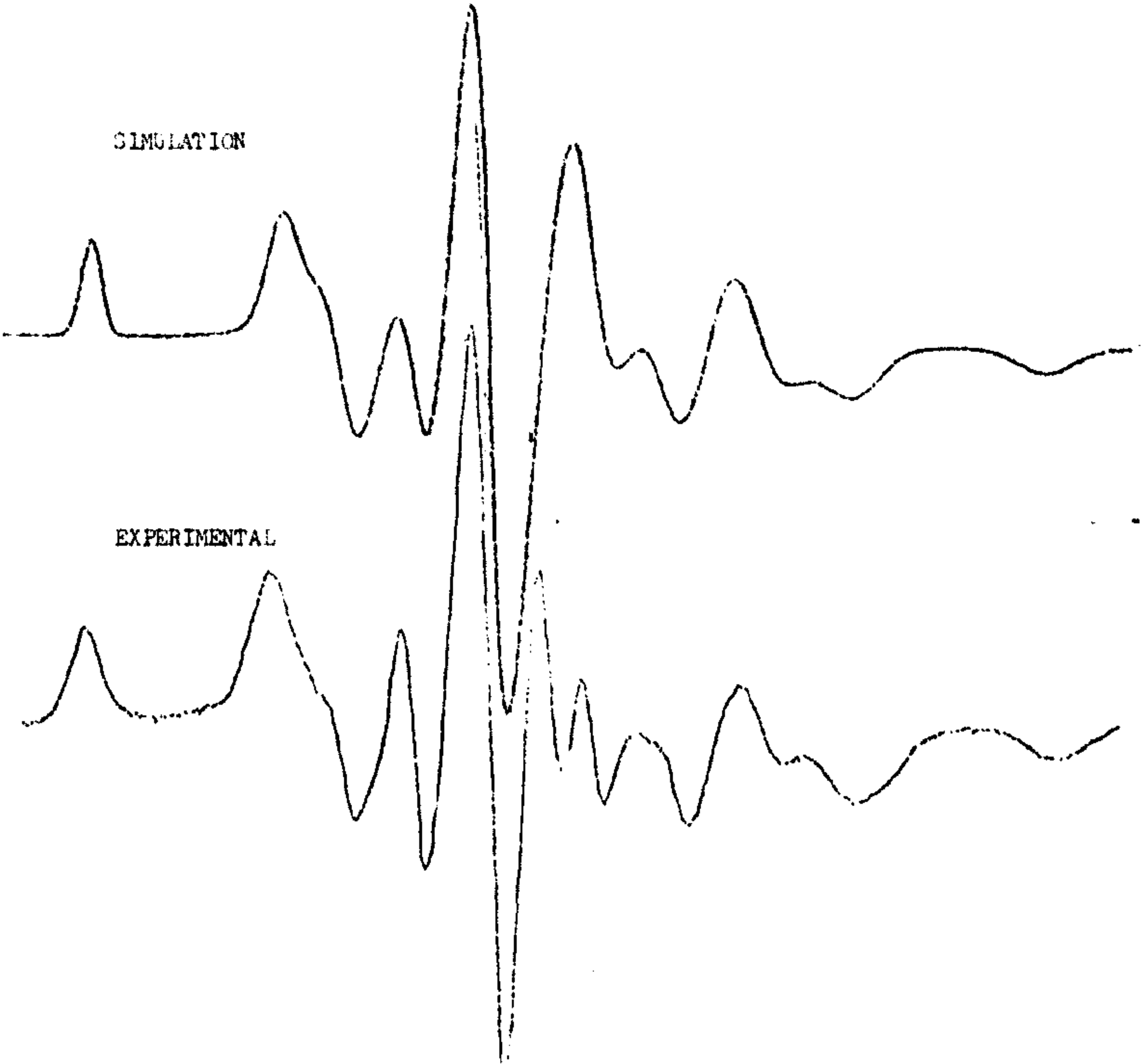
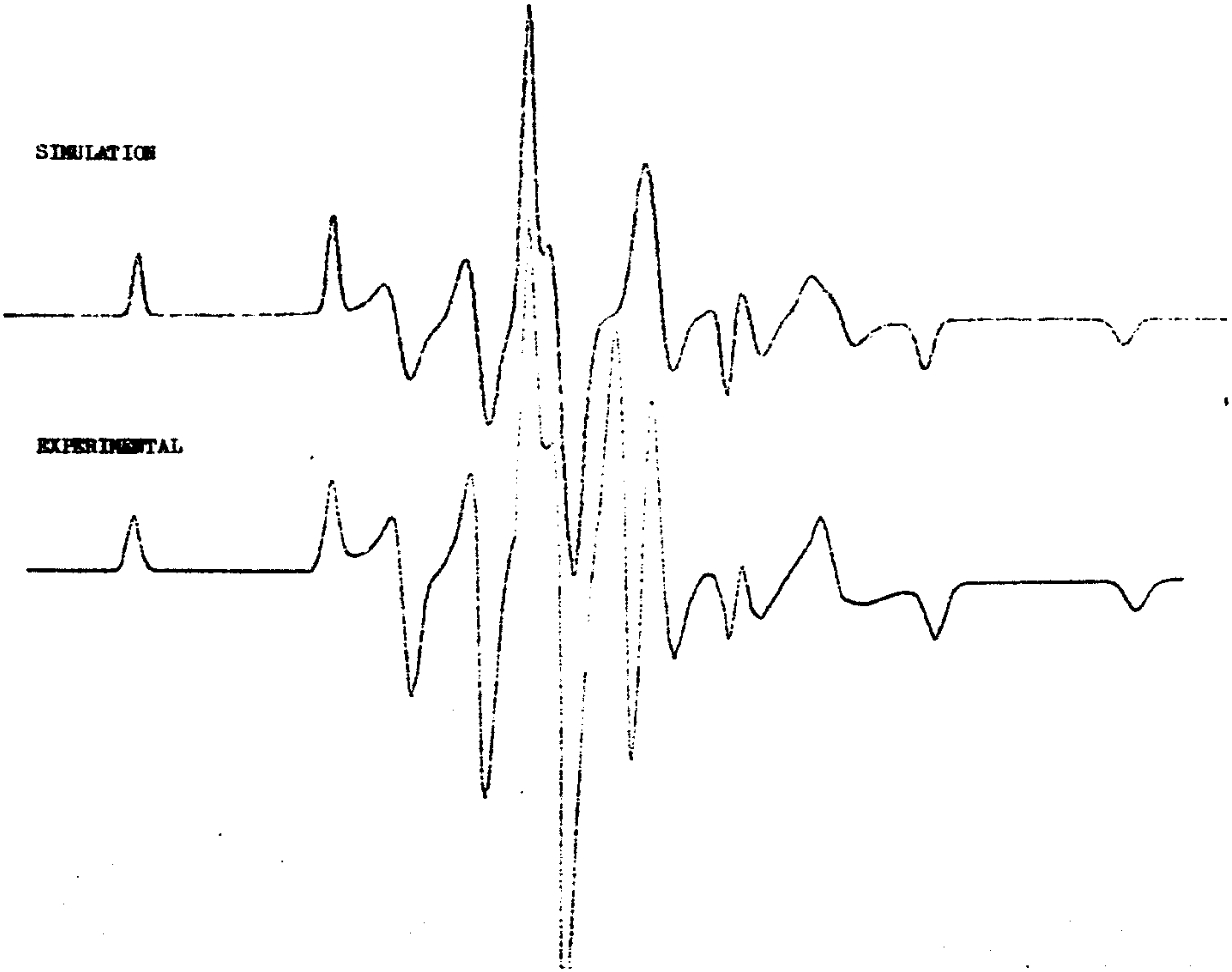

SIMULATION
EXPERIMENTAL

Figure 12. Simulation of Liczwek's ^{97}Mo X-band spectrum. (Best fit parameters listed in Table IV).


SIMULATION
EXPERIMENTAL

see that the disparity between the spectra and the simulation in Liczwek's study stems from the failure to take the effect of the quadrupole coupling into account. This disparity is also found in Liczwek's simulation for the X-band (Figure 14). I claim that this will also be eliminated when one includes the effect of the quadrupole coupling. On the basis of the above discussion, it appears that ^{97}Mo spectrum contains a significant quadrupole contribution and that the optimum value of QD is 4.0 MHz.

4. Conclusion

The EPR spectrum of naturally abundant molybdenum in $Mo(Et_2dtc)_4Cl$ contains a big, fat spin zero peak which predominantly shadows some ^{95}Mo and ^{97}Mo peaks. However, this spectrum shows better resolved ^{95}Mo and ^{97}Mo peaks than Maurice's spectrum and certainly shows some quadrupole coupling contributions.

Althugh the same computer program and the same parameters were used for simulation, the simulation features look little different (Figure 15). The version of the program used in Liczwek's study and one in this paper were carefully checked, but no significant difference was found except some minor changes which are irrelevant. Since the difference seemed to be minor, due to limitations of time, the study was completed without exploring the consequences of those minor differences in detail.

The simulation of the ^{95}Mo spectrum done in this study did not show any significant Quadrupole coupling contribution consistent with

Figure 13. Experimental and simulation ^{97}Mo Q-band spectra by Liczwek.[13]

MISSING

PAGE (S)

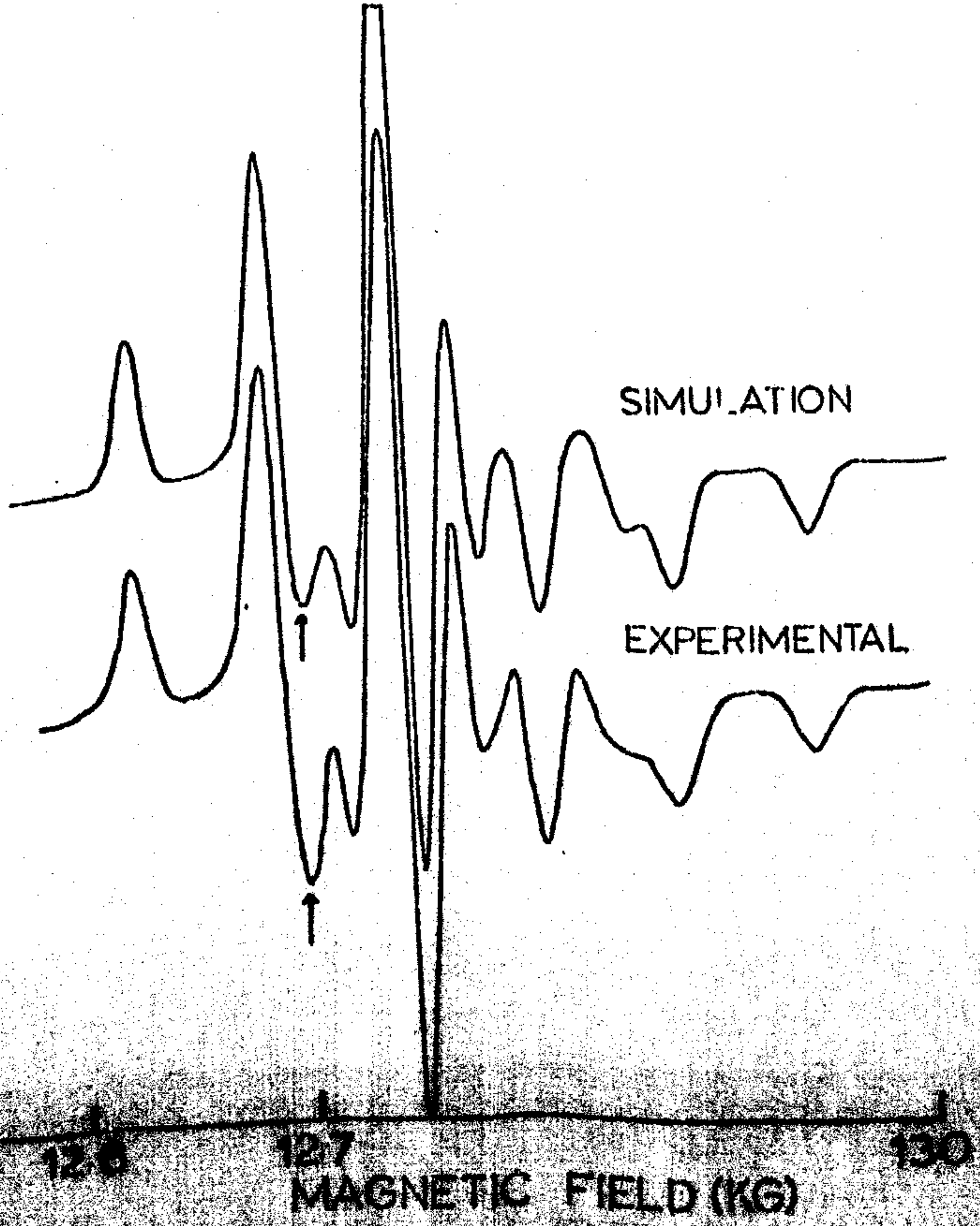

SIMULATION
EXPERIMENTAL
12.6
12.7
130
MAGNETIC FIELD (KG)

Figure 14. Experimental and simulation ^{97}Mo X-band spectra by Liczwek.

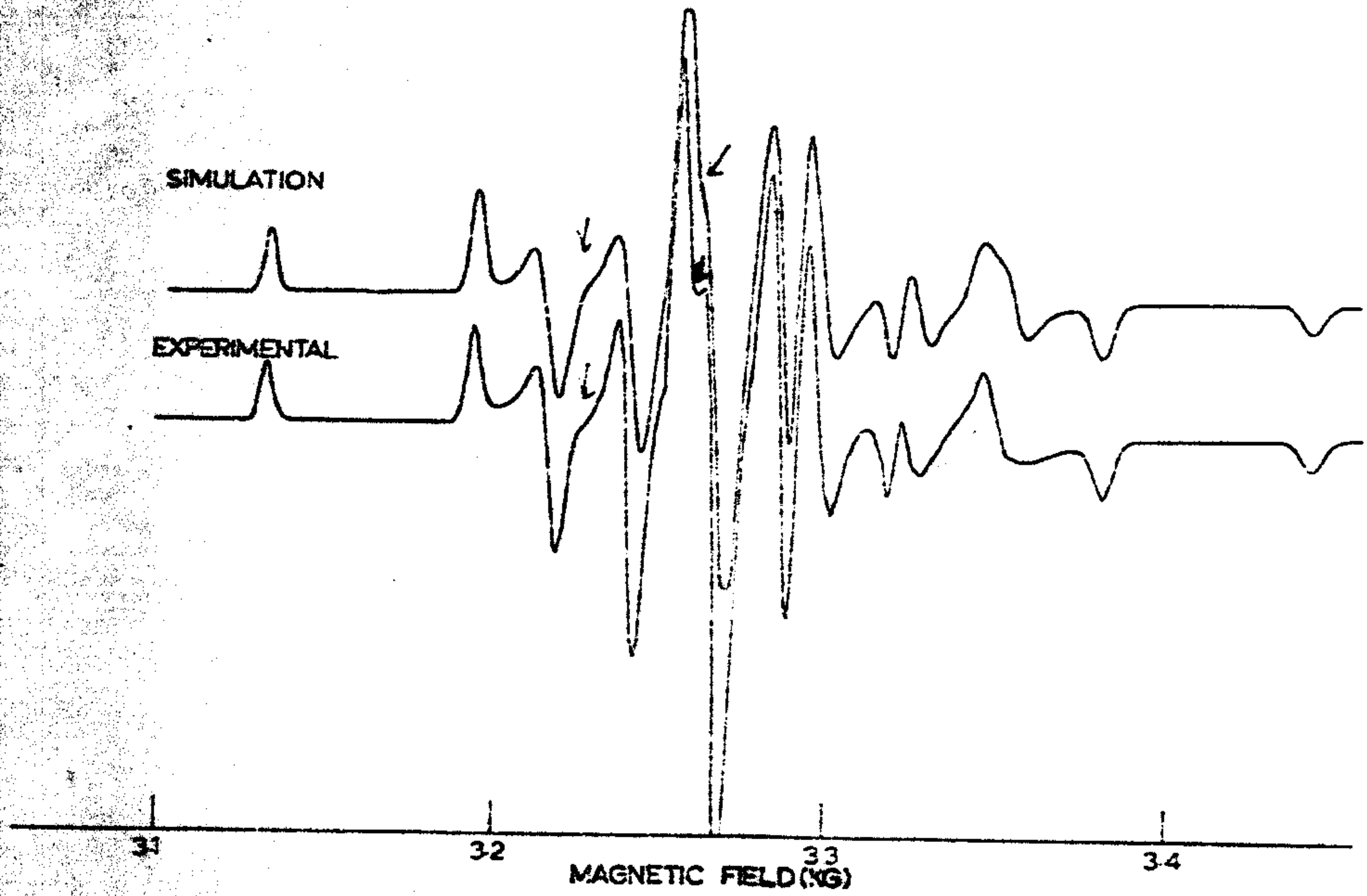
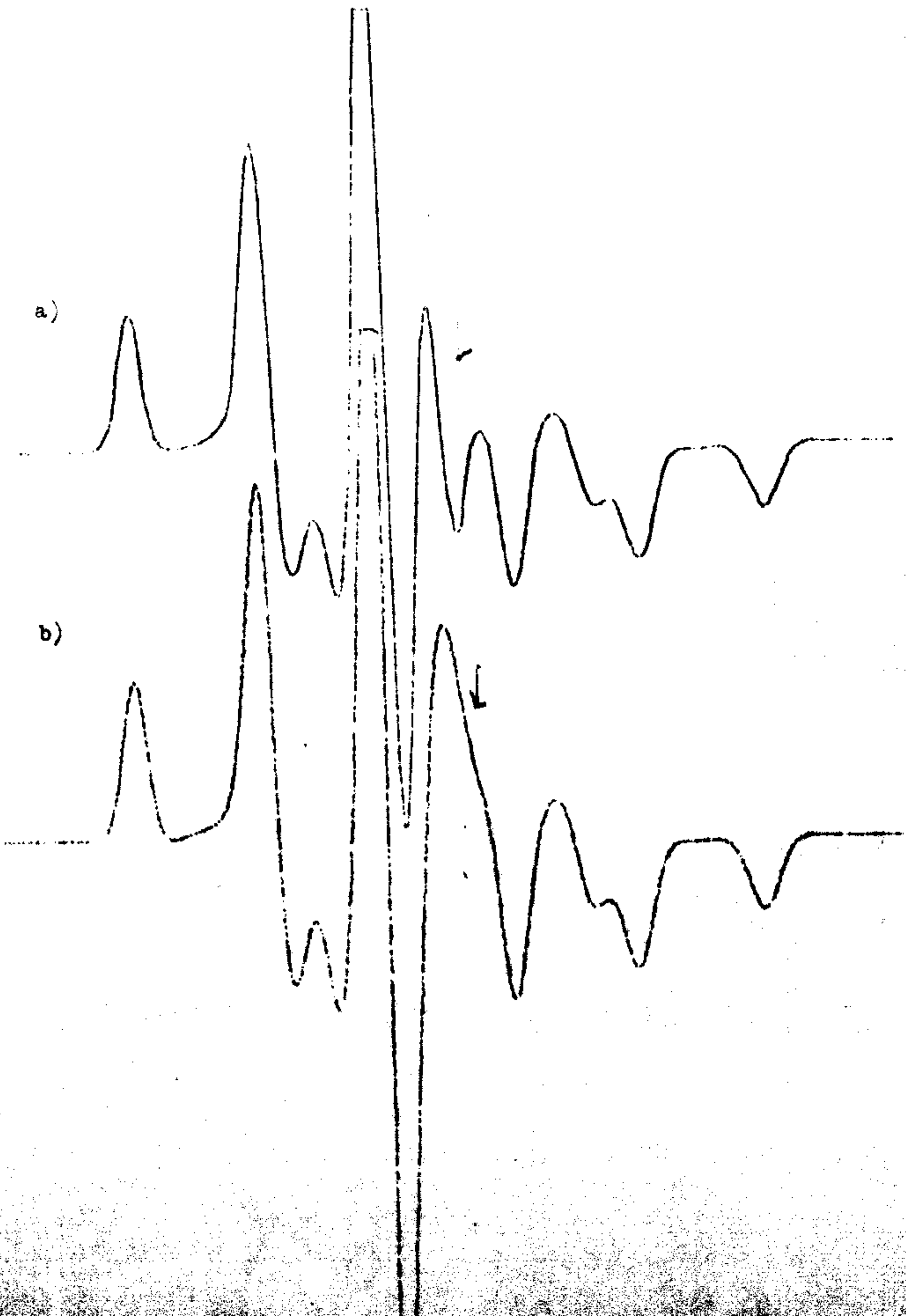

SIMULATION
EXPERIMENTAL
3.1
3.2
3.3
3.4
MAGNETIC FIELD (KG)

Figure 15. a) Simulation done by Liczwek.

b) Simulation done in this study.


a)
b)

what Liczwek and Maurice both reported. The simulation of the ^{97}Mo spectrum showed significant quadrupole coupling contribution. This result differs from that of Liczwek but is consistent with Maurice's results. The disparity between Liczwek's simulations and spectra which was eliminated in the simulation done in this study; as well, spectra of naturally abundant molybdenum simulated in this study would seem to support the results of the present study over Liczwek's.

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