

RESONANCE FLUORESCENCE OF A TWO-LEVEL ATOM NEAR A METAL 1/8
SURFACE(U) ROCHESTER UNIV NY DEPT OF CHEMISTRY
X HUANG ET AL. JUN 83 UROCHESTER/DC/83/TR-36

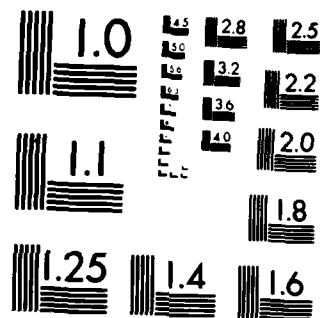
N00014-80-C-0472

NL

DATE _____

883

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

12

OFFICE OF NAVAL RESEARCH

Contract N00014-80-C-0472

Task No. NR 056-749

TECHNICAL REPORT No. 36

Resonance Fluorescence of a Two-Level
Atom Near a Metal Surface

by

Xi-Yi Huang, Jui-teng Lin and Thomas F. George

Prepared for Publication

in

Journal of Chemical Physics

Department of Chemistry
University of Rochester
Rochester, New York 14627

DTIC
S ELECTRA
JUL 13 1983
A

June 1983

Reproduction in whole or in part is permitted for any
purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

83 07 12 063

AD A130277

DTIC FILE COPY

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER UROCHESTER/DC/83/TR-36	2. GOVT ACCESSION NO. A130277	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Resonance Fluorescence of a Two-Level Atom Near a Metal Surface		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) Xi-Yi Huang, Jui-teng Lin and <u>Thomas F. George</u>		6. PERFORMING ORG. REPORT NUMBER
8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0472		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 056-749
10. CONTROLLING OFFICE NAME AND ADDRESS Department of Chemistry University of Rochester Rochester, New York 14627		11. REPORT DATE June 1983
12. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Code 472 Arlington, Virginia 22217		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Chemical Physics		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <div style="display: flex; justify-content: space-between;"> <div> RESONANCE FLUORESCENCE TWO-LEVEL ATOM METAL SURFACE REFLECTED FIELD POPULATION INVERSION </div> <div> POWER SPECTRUM SURFACE-DRESSED BLOCH EQUATIONS LASER BANDWIDTH PHASE-DIFFUSION MODEL OSCILLATORY BEHAVIOR </div> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A derivation of surface-dressed optical Bloch equations, involving a treatment of surface-reflected photons and a surface plasmon resonance, is presented for a collision-damped two-level atom near or adsorbed on a metal surface. Effects of the laser bandwidth are included by means of a phase-diffusion model for the driving field. In the weak-field or large detuning limit, the population inversion and resonance fluorescence spectrum are obtained analytically. These quantities along with the surface-induced phase-decay constant of the adatom show strong oscillatory behavior as a function of the adatom-surface distance.		

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

RESONANCE FLUORESCENCE OF A TWO-LEVEL ATOM NEAR A METAL SURFACE

Xi-Yi Huang,^{(a)*} Jui-teng Lin^(b) and Thomas F. George^(a)

(a) Department of Chemistry, University of Rochester
Rochester, New York 14627

(b) Laser Physics Branch, Optical Sciences Division, Naval Research Laboratory
Washington, D.C. 20375

Abstract

→ A derivation of surface-dressed optical Bloch equations, involving a treatment of surface-reflected photons and a surface plasmon resonance, is presented for a collision-damped two-level atom near or adsorbed on a metal surface. Effects of the laser bandwidth are included by means of a phase-diffusion model for the driving field. In the weak-field or large detuning limit, the population inversion and resonance fluorescence spectrum are obtained analytically. These quantities along with the surface-induced phase-decay constant of the adatom show strong oscillatory behavior as a function of the adatom-surface distance. ←

*Permanent address: Institute of Physics, Academia Sinica, Beijing (Peking), The People's Republic of China.



Wor

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64

65

66

67

68

69

70

71

72

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

92

93

94

95

96

97

98

99

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

133

134

135

136

137

138

139

140

141

142

143

144

145

146

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

218

219

220

221

222

223

224

225

226

227

228

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

253

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

294

295

296

297

298

299

300

301

302

303

304

305

306

307

308

309

310

311

312

313

314

315

316

317

318

319

320

321

322

323

324

325

326

327

328

329

330

331

332

333

334

335

336

337

338

339

340

341

342

343

344

345

346

347

348

349

350

351

352

353

354

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

372

373

374

375

376

377

378

379

380

381

382

383

384

385

386

387

388

389

390

391

392

393

394

395

396

397

398

399

400

401

402

403

404

405

406

407

408

409

410

411

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429

430

431

432

433

434

435

436

437

438

439

440

441

442

443

444

445

446

447

448

449

450

451

452

453

454

455

456

457

458

459

460

461

462

463

464

465

466

467

468

469

470

471

472

473

474

475

476

477

478

479

480

481

482

483

484

485

486

487

488

489

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

506

507

508

509

510

511

512

513

514

515

516

517

518

519

520

521

522

523

524

525

I. Introduction

Recently there has been considerable interest in the interaction of electromagnetic radiation with surfaces. The experiments which have motivated this present paper are those demonstrating the high intensity of light inelastically scattered from molecules adsorbed on metal surfaces¹ and the surface-enhanced luminescence of an excited molecule fluorescing near or on metals and dielectric fibers.²⁻⁴

To investigate the basic behavior of the surface-enhanced resonance excitation of a laser-driven quantum system near or adsorbed on a surface, as a first step we calculate the resonance fluorescence spectrum of a two-level atom near or adsorbed on a metal surface. In the surface-free case, i.e., in the absence of a solid surface or when the atom is very far from the surface, resonance excitation of a two-level atom by a laser field has been extensively investigated, using the powerful optical Bloch equations.⁵ There has also been interest in surface-enhanced spontaneous emission of two-level atoms near a mirror.⁶⁻⁹ In this paper, we provide a derivation of the surface-dressed optical Bloch equations. The following factors are taken into account:

- i) Radiative spontaneous decay and stimulated emission produced by both the driving laser field and the reflected electromagnetic field.
- ii) Collisional dephasing of the two-level atom produced by foreign atoms in the gas medium, which constitutes the half region of the interface.
- iii) The oscillatory behavior of the lifetime of the adatom due to interference between the driving field and the reflected field.

- iv) Surface-induced dephasing of the adatomic transition dipole.
- v) The interaction between the adatom and surface plasmons.
- vi) The random phase fluctuation of the laser field and its influence on the spectrum.

In Section II we derive the surface-dressed optical Bloch equations. In Section III we solve the equations in the weak-field limit to obtain the population inversion and the resonance fluorescence spectrum. In Section IV we present results for these quantities and the surface-induced phase-decay constant of the adatom. Section V is the Summary.

II. Surface-Dressed Optical Bloch Equations (SBE)

Let us consider a laser-driven two-level atom near or adsorbed on a metal surface. Although the atom has no dipole moment in its ground state, it can have a significant transition dipole connecting the ground and excited states. The reflected field provided by a metallic mirror and surface plasmon resonance can influence the dynamic behavior and scattering spectrum of the adatom.

To treat this problem we utilize a self-consistent approach. This first involves the determination of the induced transition dipole by quantum mechanics, i.e., the optical Bloch equations. The transition dipole is then used in Maxwell's equations to determine the reflected field, and the reflected field in turn is used in the quantum mechanical procedure to find the transition dipole. The resulting form of the reflected field $\hat{E}_R(t)$ is

$$\hat{E}_R(t) = \nu_{12}\hat{\sigma}_{12}(t)f(d) + \nu_{21}\hat{\sigma}_{21}(t)f^*(d), \quad (1)$$

where d is the distance between the adatom and surface, μ_{ij} is the electric-dipole transition matrix element between the states $|i\rangle$ and $|j\rangle$, $\sigma_{ij} \equiv |i\rangle\langle j|$ is the adatomic transition operator, and $f(d)$ is a distance-dependent function which will be discussed in more detail later. The SBE in operator form are then given by (assuming the equilibrium condition $\hat{W} = -1$)

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\sigma}_{21}(t) = & (i\omega_{21} - \gamma_2) \hat{\sigma}_{21}(t) + i \frac{\mu_{21}}{\hbar} \hat{W}(\hat{E}(t) + [f(d)\mu_{12}\hat{\sigma}_{12}(t) \\ & + f^*(d)\mu_{21}\hat{\sigma}_{21}(t)]) \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial}{\partial t} \hat{W}(t) = & -\gamma[1 + \hat{W}(t)] + 2i \frac{\mu_{21}}{\hbar} \hat{\sigma}_{21}(\hat{E}(t) + [f(d)\mu_{12}\hat{\sigma}_{12}(t) \\ & + f^*(d)\mu_{21}\hat{\sigma}_{21}(t)]) - 2i \frac{\mu_{12}}{\hbar} \hat{\sigma}_{12}(\hat{E}(t) + [f(d)\mu_{12}\hat{\sigma}_{12}(t) \\ & + f^*(d)\mu_{21}\hat{\sigma}_{21}(t)]) \end{aligned} \quad (3)$$

$$\frac{\partial}{\partial t} \hat{\sigma}_{12}(t) = \frac{\partial}{\partial t} \hat{\sigma}_{21}^\dagger(t), \quad (4)$$

where ω_{21} is the adatomic transition frequency, $\hat{E}(t)$ is the random phase-fluctuating electric field strength operator, γ_1 is the population relaxation constant, γ_2 is the phase relaxation constant, and $\hat{W}(t) \equiv \hat{\sigma}_{22}(t) - \hat{\sigma}_{11}(t)$ is the population inversion of the adatom. Collisions of the adatom with other atoms in the gas medium are accounted for in the impact limit by assuming $\gamma_1 \neq 2\gamma_2$.

The quantum equations of motion for \hat{W} , $\hat{\sigma}_{12}$ and $\hat{\sigma}_{21}$ are most useful in the rotating-wave approximation (RWA). By defining

$$\hat{S}_{12}(t) \equiv \hat{\sigma}_{12}(t)e^{i\omega_L t} \quad (5)$$

$$\hat{S}_{21}(t) \equiv \hat{\sigma}_{21}(t)e^{-i\omega_L t}, \quad (6)$$

where ω_L is the laser frequency, we can rewrite Eq. (2.2) within the RWA as

$$\frac{d}{dt} \begin{bmatrix} \hat{S}_{21}(t) \\ \hat{W}(t) \\ \hat{S}_{12}(t) \end{bmatrix} = \begin{bmatrix} -\tilde{\gamma}_2 + i\Delta & i\Omega^-(t)/2 & 0 \\ i\Omega^+(t) & -\gamma_1 & -i\Omega^-(t) \\ 0 & -i\Omega^+(t)/2 & -\tilde{\gamma}_2 - i\Delta \end{bmatrix} \begin{bmatrix} \hat{S}_{21}(t) \\ \hat{W}(t) \\ \hat{S}_{12}(t) \end{bmatrix} - \gamma_1 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}. \quad (7)$$

$\Omega^\pm(t) \equiv \Omega \exp[\mp i\phi(t)]$ is the time-dependent Rabi frequency, where $\Omega \equiv \frac{2}{\hbar} |\mu_{21}| E_0(t)$ and $E(t)$ is written as an expectation value in a coherent state of the laser field in terms of the phase factor $\phi(t)$ as $E(t) = E_0(t) \exp[-i\omega_L t + i\phi(t)] + \text{c.c.}$; $\Delta \equiv \omega_{21} - \omega_L$ is the detuning; the surface-induced phase-decay constant is $\gamma_\Delta \equiv \frac{2}{\hbar} \text{Im}(f) |\mu_{12}|^2$; and $\tilde{\gamma}_2 = \gamma_2 + \gamma_\Delta$.

To calculate γ_Δ , we must know the reflected field [Eq. (1)] or the complex function $f(d)$, which can be determined by the Sommerfeld-Hertz vector procedure.² For the case of a laser-excited atom emitting near a metallic half space, the imaginary part of $f(d)$ has the following form:

$$\begin{aligned}
\text{Im}(f) = & \frac{\epsilon_2}{1+\epsilon_1} \frac{k_1^3}{\left(\omega^2 - \frac{\omega_p^2}{1+\epsilon_1}\right)^2 + \frac{\delta^2 \omega_p^4}{(1+\epsilon_1)^2 \omega^2}} \\
& \times \left\{ \frac{1}{\epsilon_1} \left[(\omega^2 - \omega_p^2)^2 + \frac{\omega_p^4 \delta^2}{\omega^2} - \epsilon_1^2 \omega^4 \right] \left[\eta \sin D - \frac{1}{D^2} \cos D \right] \right. \\
& \left. + 2\omega \delta \omega_p^2 \left[\eta \cos D + \frac{1}{D^2} \sin D \right] \right\}, \quad (8)
\end{aligned}$$

where $\epsilon_2 = 1$ and $\eta \equiv \frac{1}{3} + \frac{1}{D}$ for the case of the induced dipole oriented parallel to the surface, $\epsilon_2 = 2$ and $\eta \equiv \frac{1}{3}$ for the perpendicular case, ϵ_1 is the dielectric constant for the gas medium, $k_1 = \omega \sqrt{\epsilon_1}/c$ is the wave number, ω is the emission frequency, c is the speed of light, and $D = 2k_1 d$ is the reduced distance which is dimensionless. The Drude model¹⁰ has been used to determine the dielectric constant of the metal medium, i.e.,

$$\epsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\delta)}, \quad (9)$$

where δ is the inverse of the relaxation time and ω_p is the plasma frequency. We note that $\text{Im}(f)$ has a resonance at $\omega_{sp} = \omega_p(1 + \epsilon_1)^{-1/2}$, which is the surface plasmon frequency of the interface, so that the reflected field given by Eq. (1) involves resonance energy transfer between the adatom and the excited surface plasmon.

Eq. (8) leads to a surface-induced phase-decay constant (in the unit of Einstein's spontaneous decay constant $A \equiv \frac{4\omega_p^3}{3\hbar c} |\mu_{21}|^2$) of the following form:

$$\gamma_{\Delta} = \zeta a_0 \left[a_1 \left(n \sin D - \frac{\cos D}{D^2} \right) + a_2 \left(n \cos D + \frac{\sin D}{D^2} \right) \right], \quad (10)$$

where

$$a_0 = \frac{3}{8} \frac{1}{(1-\beta^2)^2 + (\alpha/\omega_{\Delta p})^2} \quad (11)$$

$$a_1 = (2-\beta^2)^2 + (2\alpha/\omega_{\Delta p})^2 - \beta^4 \quad (12)$$

$$a_2 = (2\beta)^2 \alpha/\omega_{\Delta p}. \quad (13)$$

$\beta \equiv \omega_L/\omega_{\Delta p}$, $\alpha \equiv \delta/\beta$, ζ and n are the same as in Eq. (8) for the parallel and perpendicular cases, and $\epsilon_1 = 1$ has been assumed so that $\omega_{\Delta p} = \omega_p/\sqrt{2}$. The above expression for γ_{Δ} can be further simplified by assuming perfect reflection, i.e., $R^{\perp} = R^{\parallel} = -1$, where R^{\parallel} is the reflection coefficient for an incident ray polarized parallel to the plane of incidence (p-polarized) and R^{\perp} is the reflection coefficient for perpendicular polarization (s-polarized). Then

$$\gamma_{\Delta} = \frac{3}{2} \zeta \left(n \sin D - \frac{\cos D}{D^2} \right). \quad (14)$$

III. Resonance Fluorescence Spectrum

In this section we consider the weak field or large detuning limit, where $W(t) \equiv \langle \hat{W}(t) \rangle = -1$. We also use the phase-diffusion model^{11,12} for the laser field in order to include the effects of the laser bandwidth γ_L :

$$\langle \langle \hat{n}^-(t_1) \hat{n}^+(t_2) \rangle \rangle = \bar{n}^2 e^{-\gamma_L |t_2 - t_1|}. \quad (15)$$

The double bracket signifies two averages: one is over the stochastic ensemble, and the other is a standard quantum mechanical average. Eq. (15) applies to a partially-coherent laser field, which is the realistic situation. Given that the atom near the metal remains more or less in its ground state, we can linearize Eq. (7) to obtain

$$\frac{d}{dt} \hat{S}_{21}(t) = -(\gamma_2 + \gamma_L - i\Delta) \hat{S}_{21}(t) - \frac{i}{2} \Omega^-(t). \quad (16)$$

To determine the population inversion, let us take the laser field to be turned on at $t = 0$ with a constant amplitude for $t \geq 0$. We then obtain the analytical form

$$\begin{aligned} W(t) = & -1 + \Omega^2 \left\{ \frac{\tilde{\gamma}_2 + \gamma_L}{\gamma_1 [(\tilde{\gamma}_2 + \gamma_L)^2 + \Delta^2]} + \frac{\gamma_1 - \tilde{\gamma}_2 - \gamma_L}{\gamma_1 [(\gamma_1 - \tilde{\gamma}_2 - \gamma_L)^2 + \Delta^2]} e^{-\gamma_1 t} \right. \\ & - \frac{[(\tilde{\gamma}_2 + \gamma_L)(\gamma_1 - \tilde{\gamma}_2 - \gamma_L) + \Delta^2] \cos(\Delta t) + \Delta(2\tilde{\gamma}_2 - 2\gamma_L - \gamma_1) \sin(\Delta t)}{[(\tilde{\gamma}_2 + \gamma_L)^2 + \Delta^2][(\gamma_1 - \tilde{\gamma}_2 - \gamma_L)^2 + \Delta^2]} \\ & \left. \times e^{-(\tilde{\gamma}_2 + \gamma_L)t} \right\}. \end{aligned} \quad (17)$$

To obtain the power spectrum of the scattered light, we must find the dipole-dipole correlation function $\langle \hat{S}_{21}(t_2) \hat{S}_{12}(t_1) \rangle$. For $t_1, t_2 \gg \gamma_1^{-1}, \gamma_2^{-1}$ this takes the form ($t_2 \geq t_1$)

$$\begin{aligned} \langle \hat{S}_{21}(t_2) \hat{S}_{12}(t_1) \rangle = & \frac{\Omega}{4} \frac{1}{(\tilde{\gamma}_2 + \gamma_L) + i\Delta} \\ & \times \frac{2(\tilde{\gamma}_2 + \gamma_L)(\tilde{\gamma}_2 - \gamma_L - i\Delta) - \gamma_1[(\tilde{\gamma}_2 + \gamma_L) - i\Delta]}{\gamma_1(\tilde{\gamma}_2 + \gamma_L - i\Delta)(\tilde{\gamma}_2 - \gamma_L - i\Delta)} e^{-(\tilde{\gamma}_2 - i\Delta)(t_2 - t_1)} \end{aligned}$$

(continued)

(continued)

$$+ \frac{\Omega^2}{4} \frac{e^{-\gamma_L(t_2-t_1)}}{(\tilde{\gamma}_2 + \gamma_L + i\Delta)(\tilde{\gamma}_2 - \gamma_L - i\Delta)}. \quad (18)$$

The corresponding power spectrum for the emitted frequency ω is given by the Fourier transform of the above equation:

$$S(\omega) = \frac{\Omega^2}{2} \frac{1}{(\tilde{\gamma}_2 + \gamma_L)^2 + \Delta^2} \left\{ \frac{1}{(\tilde{\gamma}_2 - \gamma_L)^2 + \Delta^2} \left[\frac{\gamma_L(\tilde{\gamma}_2^2 - \gamma_L^2 + \Delta^2) + 2\gamma_L\Delta(\omega - \omega_L)}{\gamma_L^2 + (\omega - \omega_L)^2} \right. \right. \\ \left. \left. - \frac{\tilde{\gamma}_2(\tilde{\gamma}_2^2 - \gamma_L^2 + \Delta^2) + 2\gamma_L\Delta(\omega - \omega_{21})}{\tilde{\gamma}_2^2 + (\omega - \omega_{21})^2} \right] + \frac{2(\tilde{\gamma}_2 + \gamma_L)\tilde{\gamma}_2}{\gamma_L[\tilde{\gamma}_2^2 + (\omega - \omega_{21})^2]} \right\} \quad (19)$$

The fluorescence spectrum of Eq. (19) generally exhibits two peaks for a surface-dressed two-level atom in a weak, partially-coherent laser field. One peak is centered at $\omega = \omega_L$, which corresponds to elastic or Rayleigh scattering, and the other near $\omega = \omega_{21}$ corresponds to inelastic scattering or fluorescence. In the surface-free case for a collisionless atom in a fully-coherent laser field ($\gamma_1 = 2\gamma_2 = A$, $\gamma_L = 0$), the above spectrum becomes a single peak,

$$S(\omega) = \frac{\pi\Omega^2/2}{(A/2)^2 + \Delta^2} \delta(\omega - \omega_L), \quad (20)$$

which is the standard result of Heitler.¹³ In general, however, the adatom suffers collisions with foreign atoms in the gas medium, so that $\gamma \neq 2\gamma_2$, and there are nonzero values for the surface-induced phase-decay constant γ_δ and the laser bandwidth γ_L . This is then responsible for the second Lorentzian peak occurring near the transition frequency ω_{21} .

IV. Results

Fig. 1 shows the time evolution of the population inversion $W(t)$ [Eq. (17)] for an atom near a metal surface for two different adatom-surface plasmon resonance conditions, $\beta \equiv \omega_L/\omega_{\delta p} = 0.5$ and $\beta = 0.9$. We have used the value of 3.5×10^{-3} for the ratio $\delta/\omega_{\delta p}$, which corresponds to a silver surface. Each curve approaches a stationary-state value, assuming that the duration of the laser pulse is much longer than the relaxation time of the adatom (characterized by γ_1^{-1} and γ_2^{-1}). The reason the values of W for the off-resonance case ($\beta = 0.5$) are less than those for the near-resonance case ($\beta = 0.9$) is that the levels of the adatom in the latter case are strongly broadened by the resonant transfer of energy between the adatom and surface plasmon, so that the population of the upper level increases. The oscillations increase and the damping due to the reflected field disappears as the adatom moves further from the surface (going from curve 1 to 3). The strong oscillations in the nearly surface-free case (curve 3) are caused by beating between the driving laser field and the "adatomic oscillator".

Fig. 2 displays the resonance fluorescence spectrum [Eq. (19)], with the Rayleigh and fluorescence peaks. The former peak in our

model is just determined by the laser bandwidth γ_L . The latter peak is strongly dependent on the adatom-surface distance; as the distance decreases, the upper adatomic level broadens and hence the fluorescence intensity increases.

In Fig. 3 we plot $W(t)$ for the case of a perfectly reflective metal surface, $R^\perp = R^\parallel = -1$ [see Eq. (14)], for several values of the laser bandwidth and adatom-surface distance. The oscillations increase as the adatom moves further from the surface and decrease as the laser bandwidth increases [going from (a) to (c)]. A larger bandwidth leads to more damping of the adatomic oscillator [see Eq. (17)] and hence an increase in the population inversion. It is interesting to note that W is more sensitive to the adatom-surface distance for the case of the transition dipole oriented parallel to the surface than for the perpendicular case. We see that the positions of the dashed curves 2 and 3 are interchanged, indicating that the power spectrum oscillates as a function of D . As seen by the form of Eq. (8), we would also see such oscillations for the population inversion and power spectrum in Figs. 1 and 2 if we were to consider a wider range of values of D .

Fig. 4 displays the surface-induced phase-decay constant γ_δ as a function of the adatom-surface distance for a perfectly reflective surface. The oscillations are due to the interference between the reflected field and the driving field. This gives rise to oscillations in the lifetime of the adatomic oscillator, while the small negative value of γ_δ in some regions of D tends to increase the lifetime.

Fig. 5 shows the power spectrum for several values of the laser bandwidth γ_L . When γ_L is very small compared to the phase-decay constant γ_2 [Fig. 5(a)],

the power is concentrated largely in the Rayleigh peak. Here the population of the upper adatomic level, and hence the power of the fluorescence, is determined mainly by the broadening of that level due to the surface, so that the power increases as D decreases. The situation is changed when γ_L is larger than γ_2 , in which case the power of the Rayleigh component transfers to the fluorescence peak [Fig. 5(b) and (c)]. Although a decrease in D leads to a broadening of the adatomic level, now the total power in the fluorescence peak is approximately unchanged, whereby a curve for smaller D has a larger width but a smaller peak height. A more detailed discussion on the relation between fluorescence and laser bandwidth in general will be published later.

It is interesting to note that Weitz et al recently published measurements and a theoretical model on a hierarchy of enhancement ratios for normal Raman scattering, resonance Raman scattering and fluorescence from molecules adsorbed on a silver surface.¹⁴ The results from our two-level adatom model for surface-enhanced fluorescence are in good agreement with their measured enhancement ratio of 10^{-1} to 10 for fluorescence.

V. Summary

A simple model has been developed to describe the dynamic behavior of a two-level adatom at a metal surface. Surface-dressed optical Bloch equations (SBE), which account for surface-reflected photons and adatom-surface plasmon coupling, have been derived. Collisions with foreign gas atoms and effects of the laser bandwidth have been included. The SBE have been used to evaluate the power spectrum of the scattered light, the population inversion and the surface-induced phase-decay constant as functions of the adatom-surface distance and adatom-surface plasmon resonance parameter β . The displayed properties of the laser-adatom-surface system should be useful in understanding basic processes occurring in surface resonance spectroscopy.

Acknowledgments

This work was supported in part by the Office of Naval Research, the Air Force Office of Scientific Research (AFSC) under Grant No. AFOSR 82-0046 and the U.S. Army Research Office. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. TFG acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1975-84) and the John Simon Guggenheim Memorial Foundation for a Fellowship (1983-84). XYH acknowledges helpful conversations with Professors S. Mukamel, L. Mandel and P. W. Milonni.

References

1. See, for example the review article by T. E. Furtak and J. Reyes, Surface Sci. 93, 351 (1980), and the references contained therein.
2. See the review by R. R. Chance, A. Prock and R. Silbey, Adv. Chem. Phys. 37, 1 (1978).
3. A. M. Glass, P. F. Liao, J. G. Bergman and D. H. Olson, Opt. Lett. 5, 368 (1980).
4. J. F. Owen, P. W. Barber, P. B. Dorain and R. K. Chang, Phys. Rev. Lett. 47, 1075 (1981).
5. L. Allen and J. H. Eberly, Optical Resonance and Two-Level Atoms (Wiley, New York, 1975).
6. V. L. Lyuboshitz, Soviet Physics JETP 26, 937 (1968).
7. H. Morawitz, Phys. Rev. 187, 1972 (1969).
8. P. W. Milonni and P. L. Knight, Opt. Commun. 9, 119 (1973).
9. G. S. Agarwal, Opt. Commun. 42, 205 (1982).

10. M. Born and W. Wolf, Principles of Optics (Pergamon, New York, 1975) pp. 624-627.
11. R. J. Glauber, in Quantum Optics and Electronics, edited by C. DeWitt A. Blandin and C. Cohen-Tannoudji (Gordon and Breach, New York, 1965), pp. 65-185.
12. J. H. Eberly, Phys. Rev. Lett. 37, 1387 (1976).
13. W. Heitler, The Quantum Theory of Radiation (Oxford, London, 1954).
14. J. H. Eberly, X. Y. Huang and G. S. Agarwal, to be published.
15. D. A. Weitz, S. Garoff, J. I. Gersten and A. Nitzan, J. Chem. Phys. 78, 5324 (1983).

Figure Captions

1. Time evolution of the population inversion in the weak field or large detuning limit, with $(\gamma_L, \Omega, \Delta) = (0.3, 0.05, 5)$ in the unit A for $\beta = 0.9$ (solid curves) and $\beta = 0.5$ (dashed curves). Curves 1, 2 and 3 correspond to the values of the reduced distance $D = 2k_1d$ of 1, 3 and 5, respectively. The horizontal axis corresponds to time in the unit A^{-1} . The quantity $[W(t)+1]/\Omega^2$ is shown along the vertical axis.
2. Fluorescence power spectrum of scattered light with $(\gamma_L, \Omega, \Delta) = (0.3, 0.05, 5)$ in the unit A and $\beta = 0.9$ for the induced transition dipole oriented perpendicular to the surface. The units along the vertical axis are arbitrary. Curves 1, 2 and 3 correspond to $D = 1, 3$ and 5 , respectively.
3. Time evolution of the population inversion $W(t)$ of an adatom at a perfectly reflective metal surface, with $\Omega = 0.05, \Delta = 5$, (a) $\gamma_L = 0.3$, (b) $\gamma_L = 1$, and (c) $\gamma_L = 3$ (in the unit A). The solid curves are for the induced transition dipole oriented perpendicular to the surface, while the dashed curves are for the parallel case, and the labels 1, 2 and 3 correspond to $D = 2, 4$ and 6 , respectively.
4. Surface-induced phase-decay constant γ_s (in the unit A) as a function of the reduced adatom-surface distance $D = 2k_1d$ for a perfectly reflective metal surface. The solid curve is for the induced transition dipole oriented perpendicular to the surface, while the dashed curve is for the parallel case.
5. Power spectrum of scattered light for a perfectly reflective metal surface, with $\Omega = 0.05, \Delta = 5$, (a) $\gamma_L = 0.3$, (b) $\gamma_L = 1$ and (c) $\gamma_L = 3$ (in the unit A). The induced transition dipole is oriented perpendicular to the surface. The units along the vertical axis are arbitrary. Curves 1, 2 and 3 correspond to $D = 2, 4$ and 6 , respectively.

Fig. 1

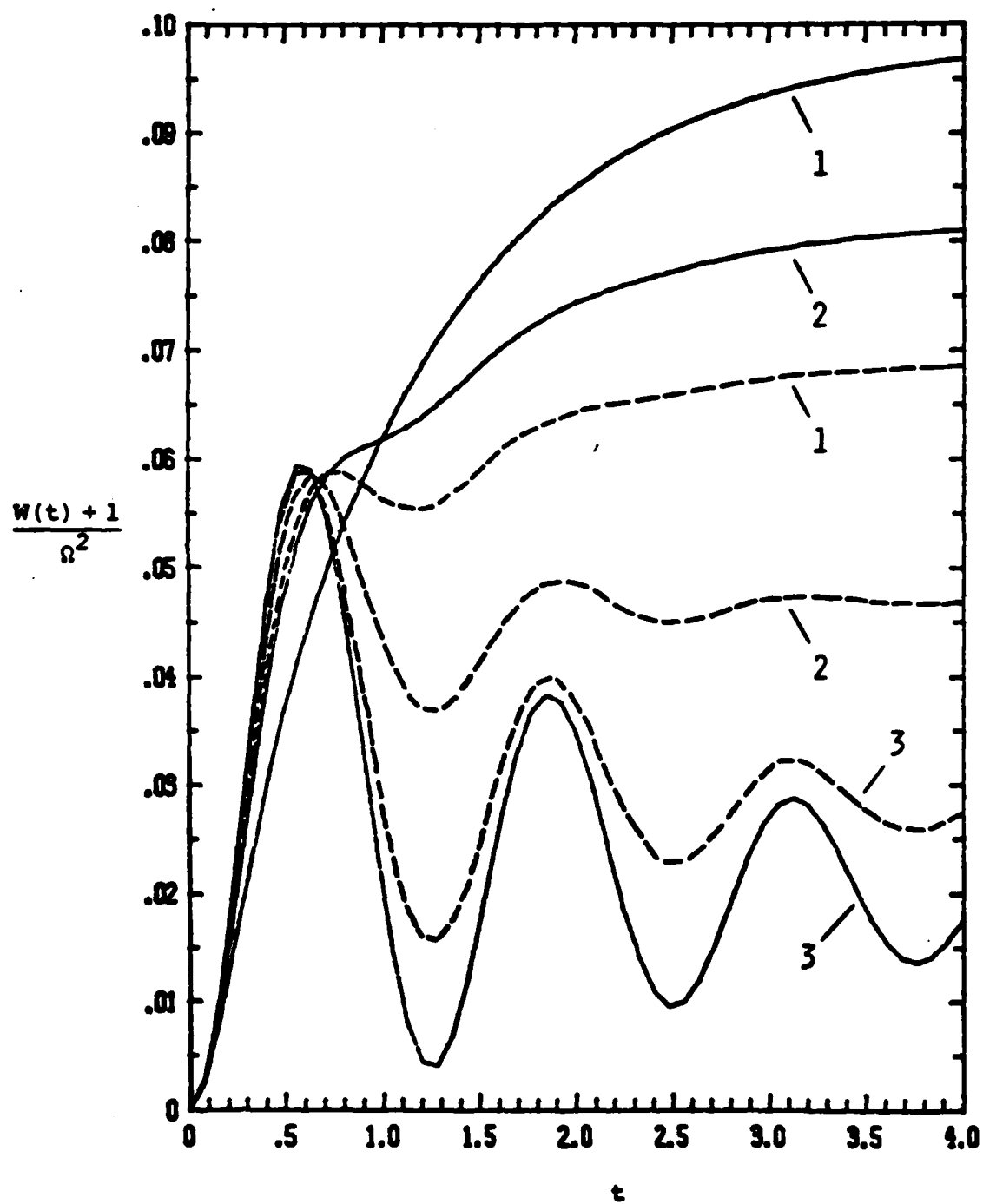


Fig. 2

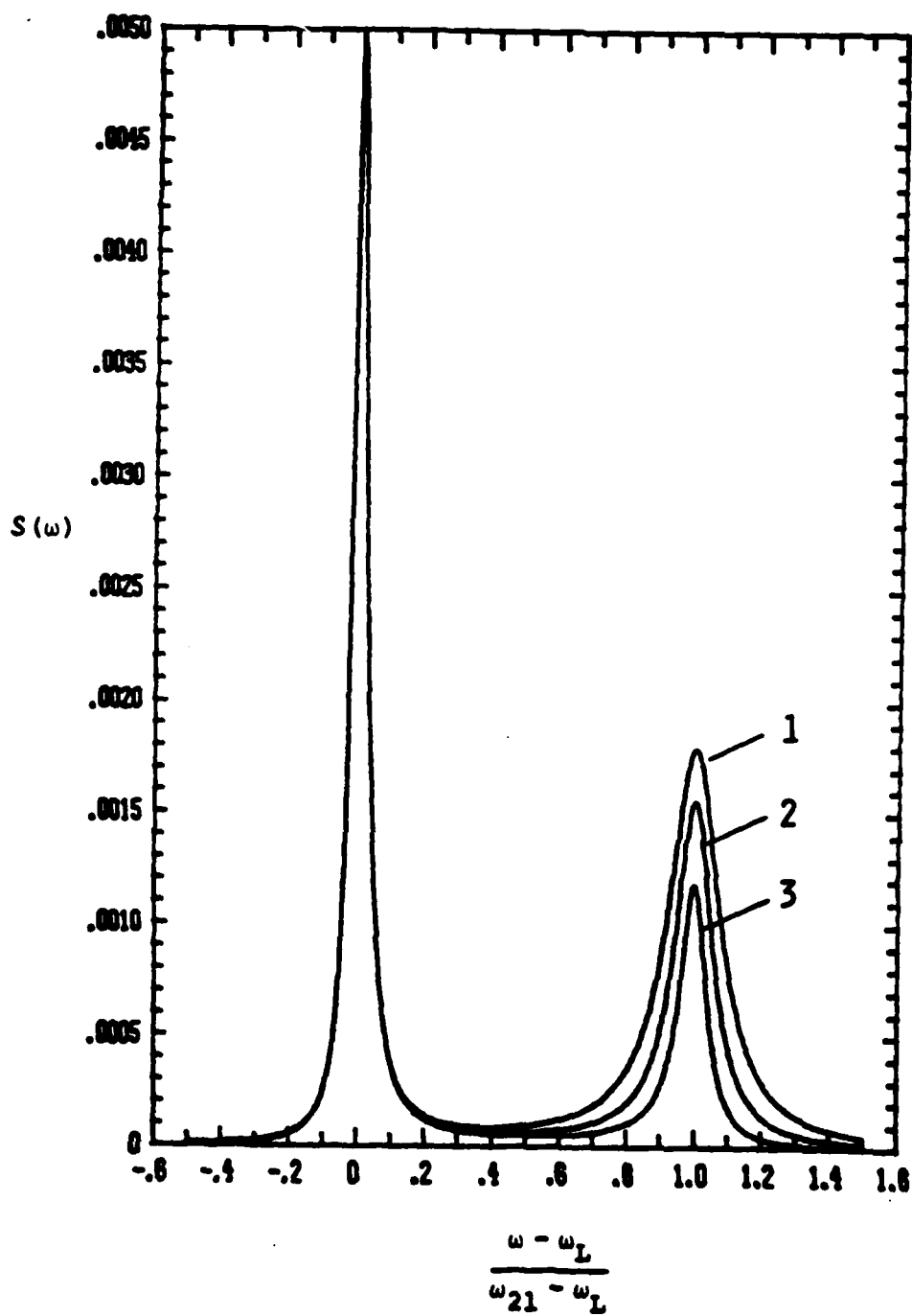


Fig. 3(a)

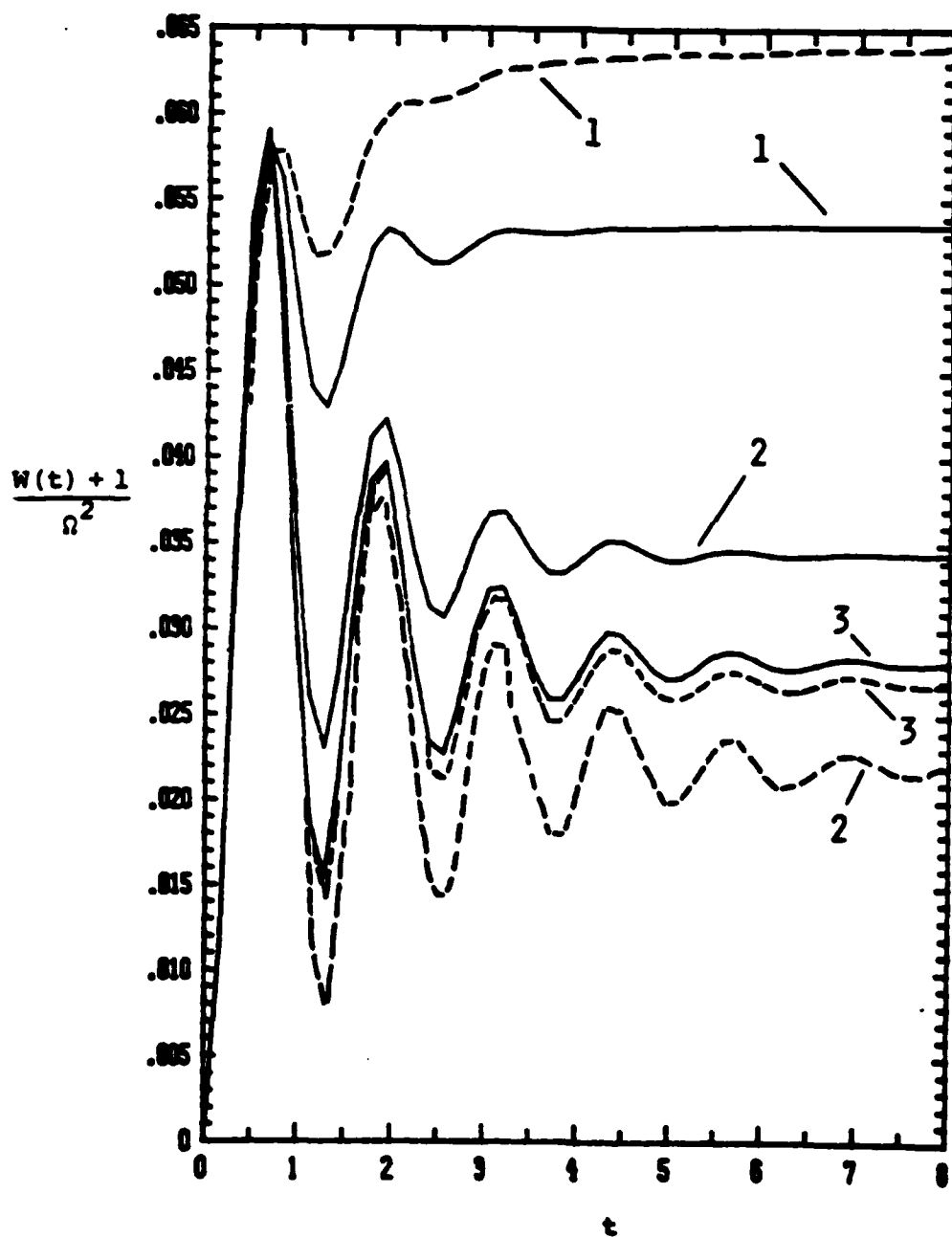


Fig. 3(l)

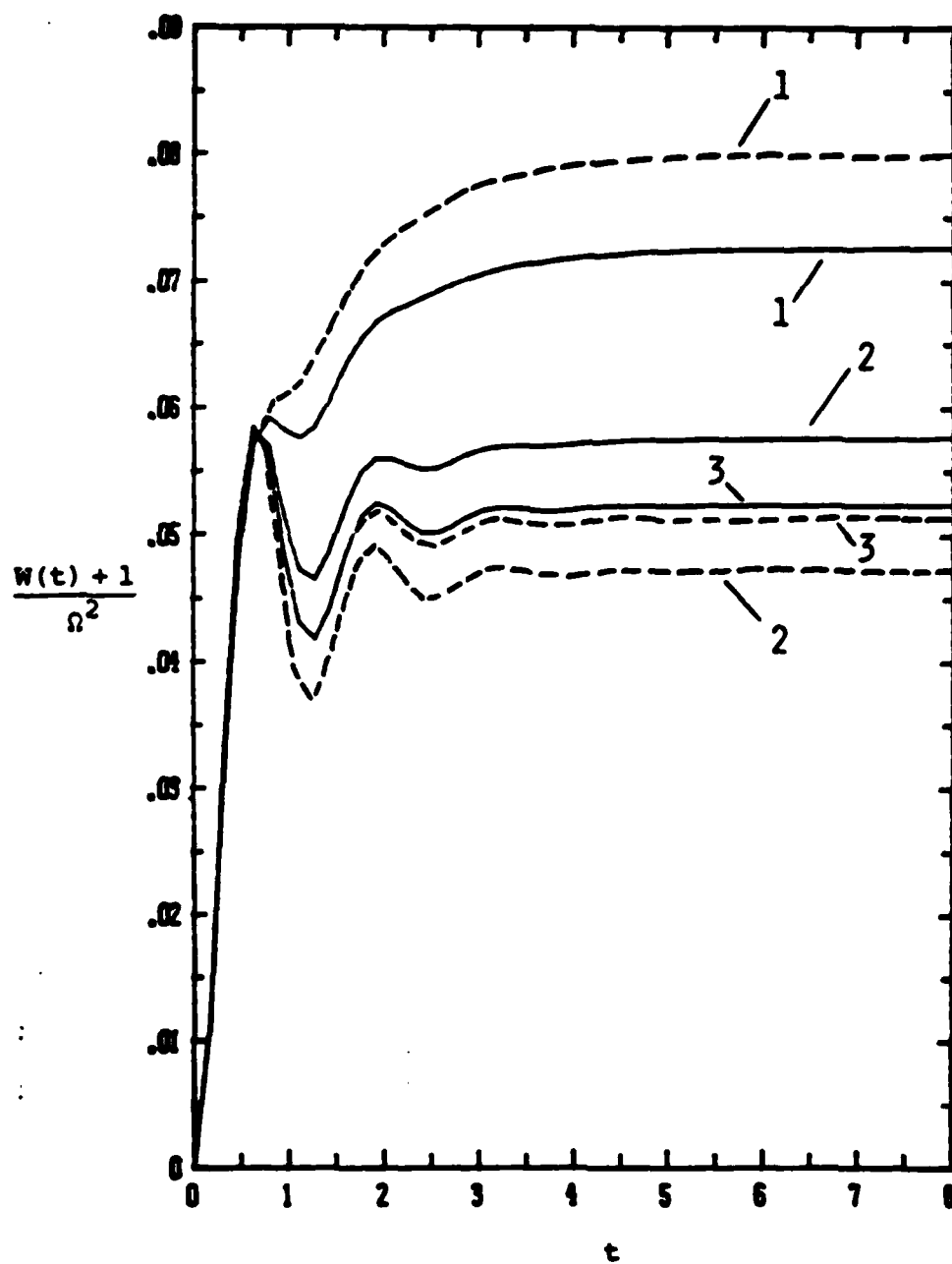


Fig. 3(c)

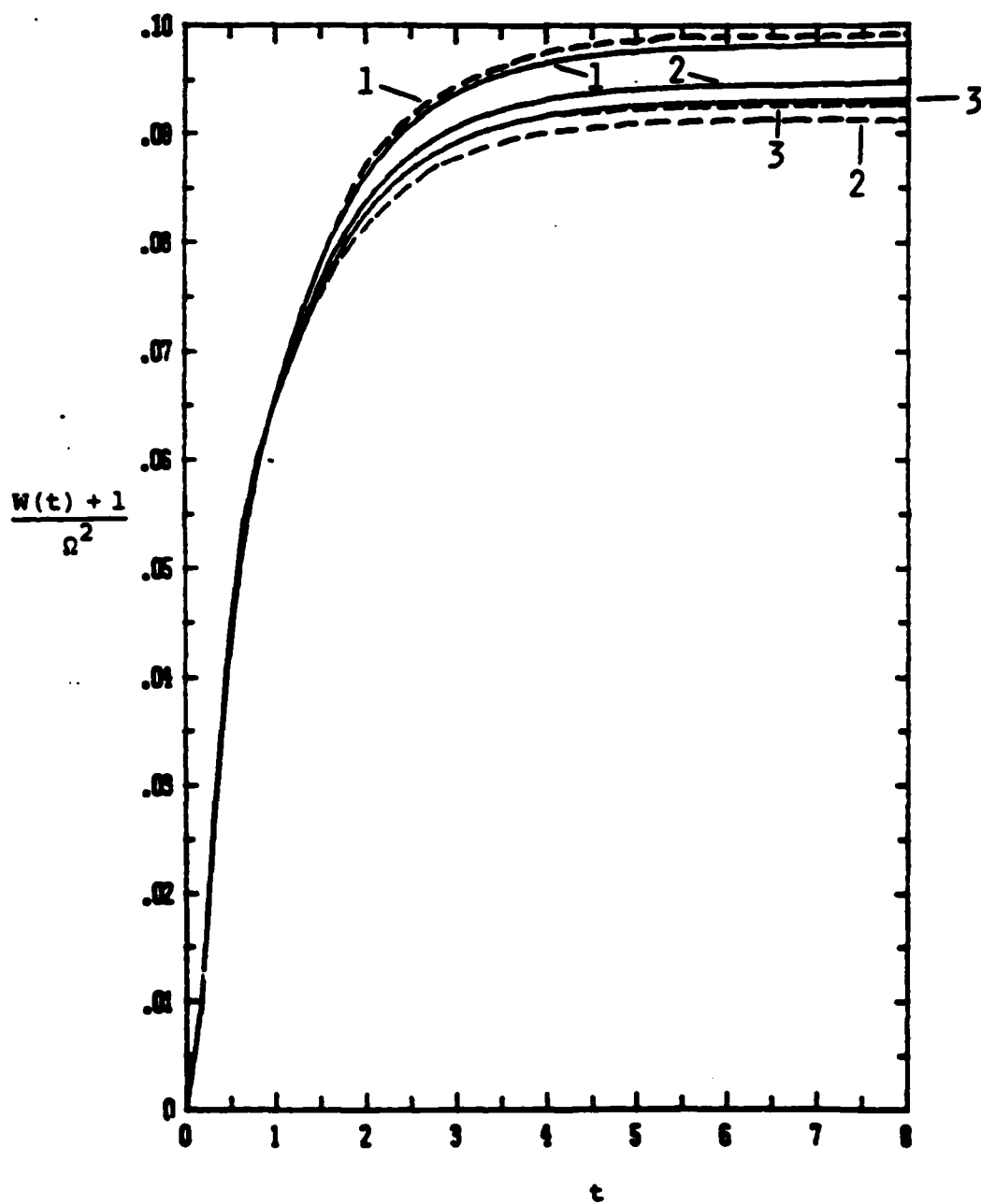


Fig. 4

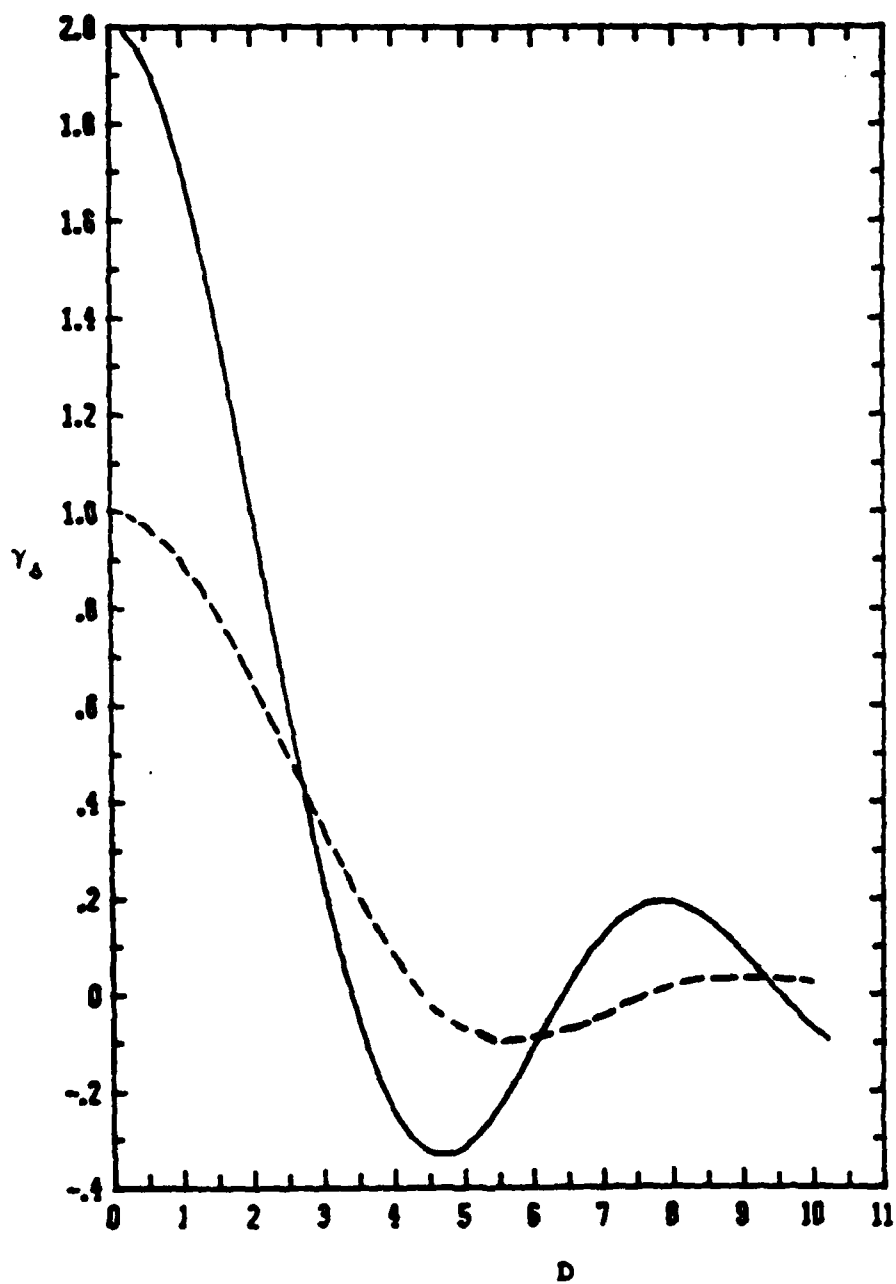


Fig. 5(a)

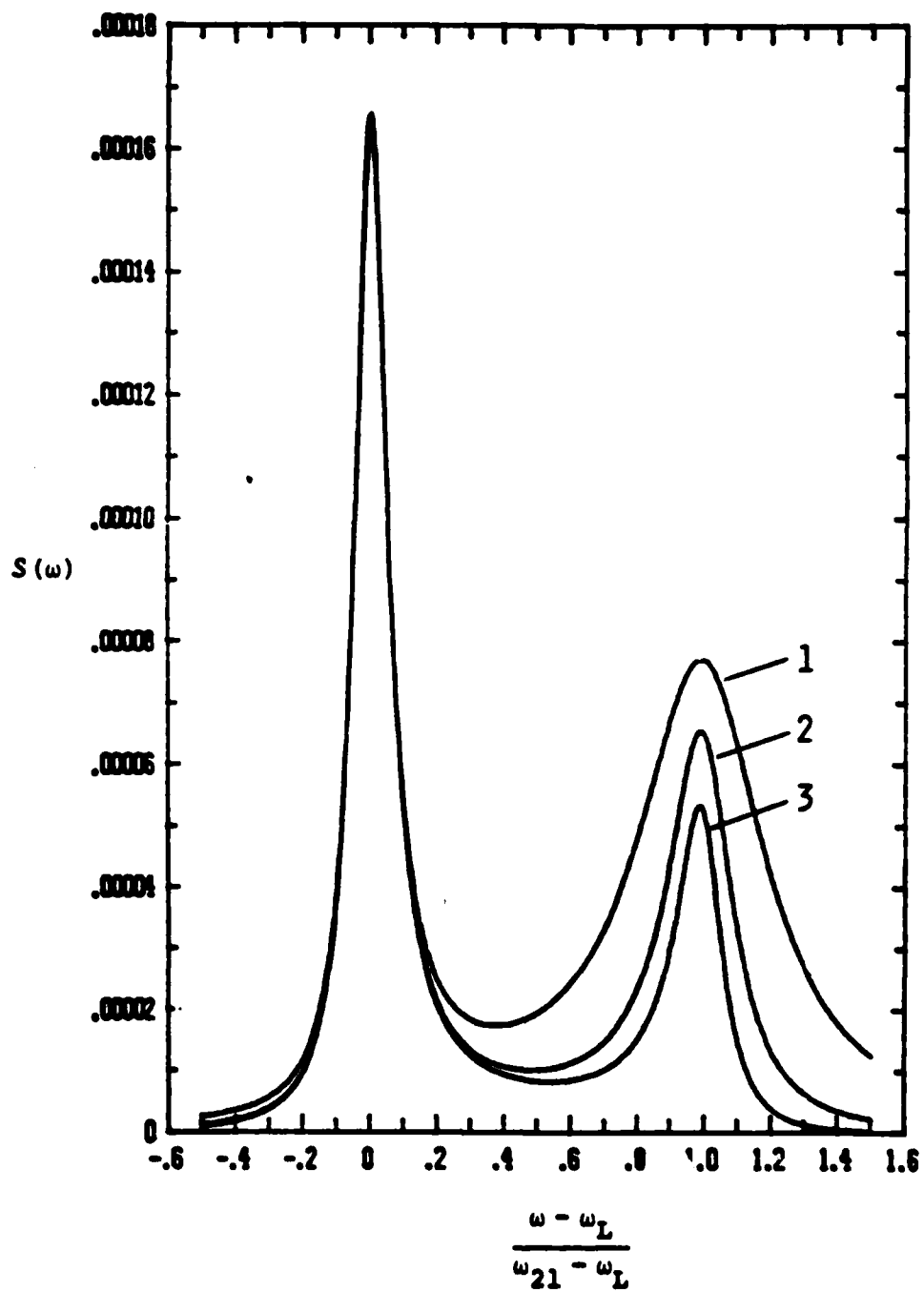


Fig. 5(b)

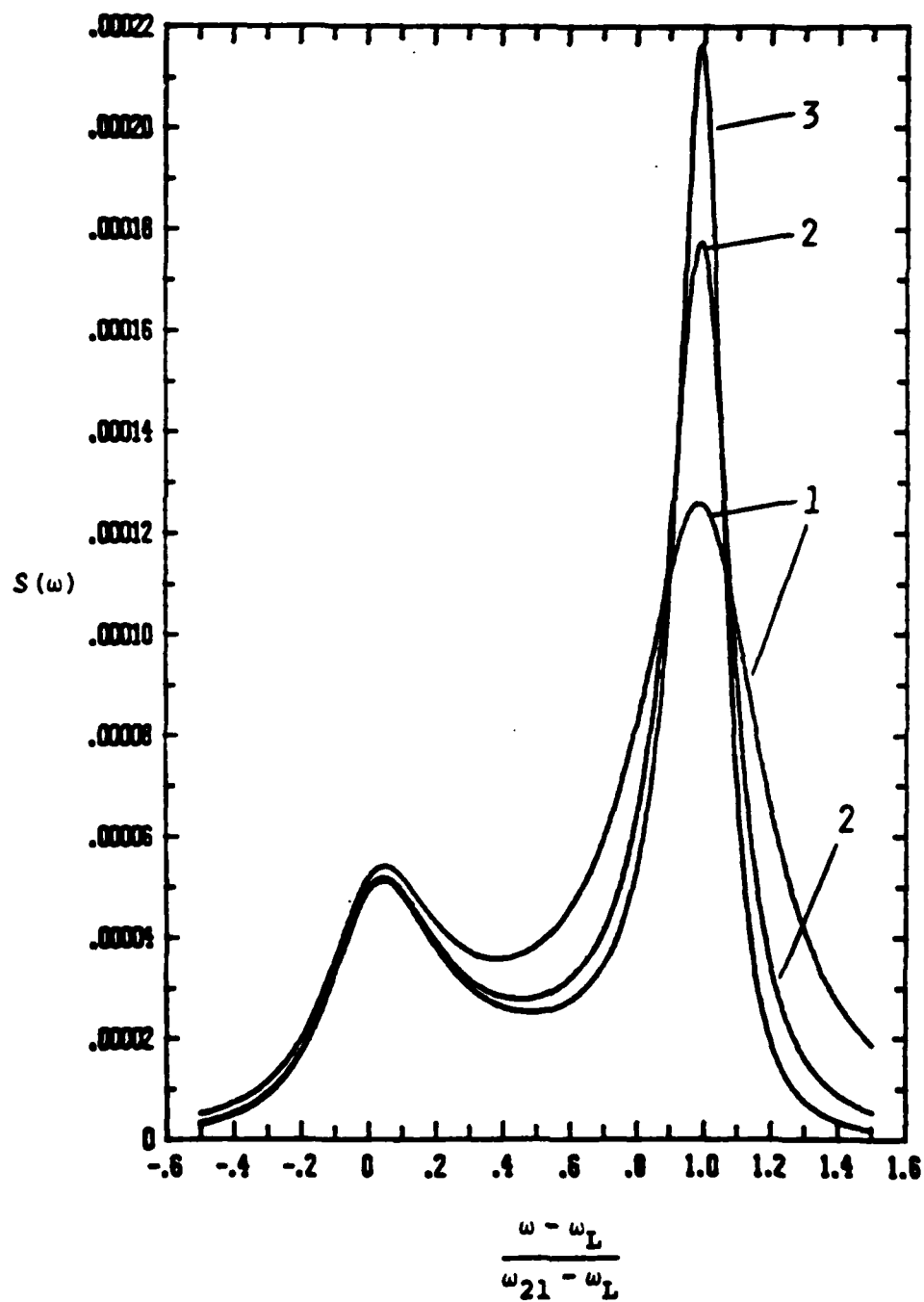
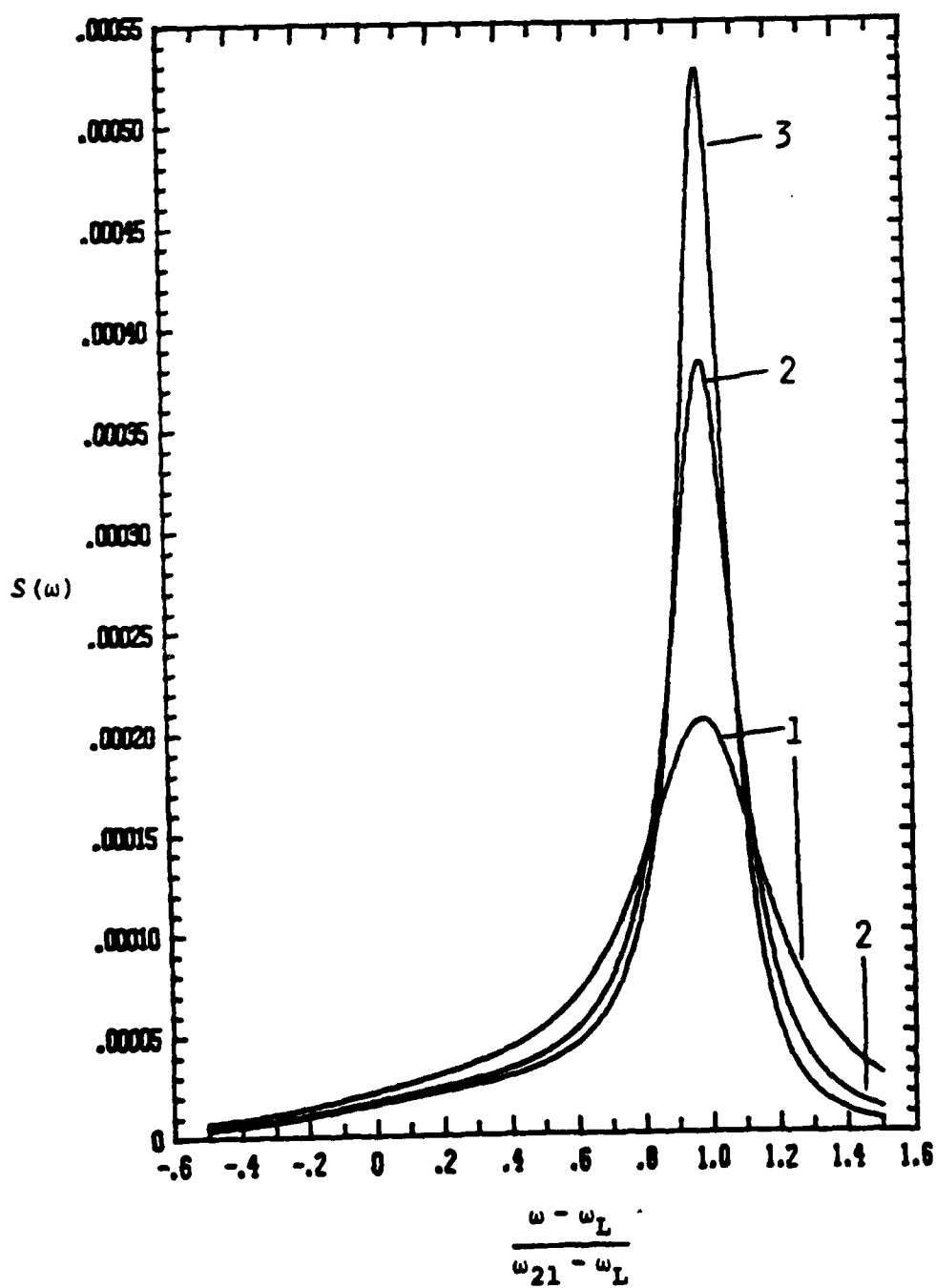


Fig. 5(c)



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 North Quincy Street Arlington, Virginia 22217	2	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Pasadena Detachment Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Dean William Tolles Naval Postgraduate School Monterey, California 93940	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P. O. Box 12211 Research Triangle Park, N.C. 27709	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Mr. Vincent Schaper DTNSRDC Code 2803 Annapolis, Maryland 21402	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1	Mr. A. M. Anzalone Administrative Librarian PLASTEC/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1
Dr. David L. Nelson Chemistry Program Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	1		

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. G. A. Somorjai Department of Chemistry University of California Berkeley, California 94720	1	Dr. W. Kohn Department of Physics University of California (San Diego) La Jolla, California 92037	1
Dr. J. Murday Naval Research Laboratory Surface Chemistry Division (6170) 455 Overlook Avenue, S.W. Washington, D.C. 20375	1	Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1
Dr. J. B. Hudson Materials Division Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. Theodore E. Madey Surface Chemistry Section Department of Commerce National Bureau of Standards Washington, D.C. 20234	1	Dr. Chia-wei Woo Department of Physics Northwestern University Evanston, Illinois 60201	1
Dr. J. M. White Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. Robert M. Hexter Department of Chemistry University of Minnesota Minneapolis, Minnesota 55455	1
Dr. Keith H. Johnson Department of Metallurgy and Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. R. P. Van Duyne Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. J. E. Demuth IBM Corporation Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1	Dr. S. Sibener Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1
Dr. C. P. Flynn Department of Physics University of Illinois Urbana, Illinois 61801	1	Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1	Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1	Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052	1	Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	1
Dr. P. Hansma Physics Department University of California, Santa Barbara Santa Barbara, California 93106	1	Professor D. Hercules University of Pittsburgh Chemistry Department Pittsburgh, Pennsylvania 15260	1
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1	Professor N. Winograd The Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton SO9 5NH Hampshire, England	1	Professor T. F. George The University of Rochester Chemistry Department Rochester, New York 14627	1
Dr. G. Rubloff IBM Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1	Professor Dudley R. Herschbach Harvard College Office for Research Contracts 1350 Massachusetts Avenue Cambridge, Massachusetts 02138	1
Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1	Professor Horia Metiu University of California, Santa Barbara Chemistry Department Santa Barbara, California 93106	1
Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1	Professor A. Steckl Rensselaer Polytechnic Institute Department of Electrical and Systems Engineering Integrated Circuits Laboratories Troy, New York 12181	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>
Dr. John T. Yates Department of Chemistry University of Pittsburgh Pittsburgh, Pennsylvania 15260	1	
Professor G. H. Morrison Department of Chemistry Cornell University Ithaca, New York 14853	1	
Captain Lee Myers AFOSR/NC Bolling AFB Washington, D.C. 20332	1	
Dr. David Squire Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709	1	
Professor Ronald Hoffman Department of Chemistry Cornell University Ithaca, New York 14853	1	

DATE
ILME